EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM SELECTED ORGANIC CHEMICAL PLANTS

for

Environment Canada
Conservation and Protection

by

B.H. Levelton & Associates Ltd.
8805 Osler Street
Vancouver, B.C.
V6P 4G1

W.C. Edwards, P.Eng.
R.G. Quan, P.Eng.
N.P. Lee, P.Eng.

October 1990

IP-118
November 1990

92-00339/

EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM SELECTED ORGANIC CHEMICAL PLANTS

Prepared for

Environment Canada

by

W.C. Edwards, R.G. Quan and N.P. Lee
B.H. Levelton & Associates Ltd.
Vancouver, B.C.

This report has not undergone detailed technical review by the Conservation and Protection Service and the content does not necessarily reflect the views and policies of Environment Canada. Mention of trade names or commercial products does not constitute endorsement for use.

This unedited version is undergoing a limited distribution to transfer the information to people working in related studies. This distribution is not intended to signify publication and, if the report is referenced, the author should cite it as an unpublished report of the Branch indicated below.

Any comments concerning its content should be directed to:

Industrial Programs Branch
Environmental Protection Directorate
Conservation and Protection
Environment Canada
Ottawa, Ontario
K1A 0H3

ACKNOWLEDGEMENT

This study was completed with extensive guidance from Art Stelzig, Fred Chen, Frank Vena and Tony Kosteltz of Conservation and Protection, Environment Canada, Hull, Quebec, and their assistance is very much appreciated.

The authors would also like to acknowledge the cooperation of the member companies of the Canadian Chemical Producers Association which participated in this survey and provided the detailed data essential for preparation of the VOC inventory. The members of the CCPA VOC Task Force, which was formed to coordinate and contribute to this study, are as follows:

Co-Chairmen

Mr. D. Bisset
Shell Canada Ltd.

Mr. A. Stelzig
Environment Canada

Participants

Dow Chemical Canada Inc. Sarnia, Ontario Fort Saskatchewan, Alberta	 Mr. I. McGuiness Mr. S. Penttinen
Polysar Ltd. (Nova Petrochemicals Inc.) Sarnia, Ontario	Mr. A. Dunlop Mr. M. Marcinkowski
Novacor Chemicals Ltd. Joffre, Alberta Moore Township, Ontario	 Mr. D. Wurster Mr. J. Tiernay
Esso Chemical Canada Sarnia, Ontario	Mr. J. Johnston Mr. A. Catalano Mr. J. Rogers
Suncor Inc. Sarnia, Ontario	Mr. J. Greenshields
Monsanto Canada Inc. LaSalle, Quebec	Ms. M. Gilbert

Shell Canada Ltd. Fort Saskatchewan, Alberta	Mr. R. Leflar
Dupont Canada Inc. Corunna, Ontario	Mr. D. Newman
Union Carbide Canada Ltd. Montreal-East, Quebec Prentiss, Alberta	Mr. L. Hamel Mr. C. Sam
Carbochem Inc. Hamilton, Ontario	Mr. W. Lutek
Petromont Inc. Varennes, Quebec	Mr. A. Charron

CCPA Consultant

H.W. Quinn

TABLE OF CONTENTS

ACKNOWLEDGEMENT i

I. INTRODUCTION 1

A. Background 1

B. Scope of Work 4

II. INVENTORY METHODOLOGY 6

A. Types of VOC Sources 6

B. Approach to Inventory Methodology Development 7

C. Process Sources 8

D. Fugitive Sources 10

E. Storage and Loading Sources 14

F. Spills and Accidental Discharges to the Atmosphere 16

III. EMISSIONS OF VOLATILE ORGANIC COMPOUNDS 17

A. Plants Included in the Inventory 17

B. Emissions by Product and Source Type 18

1. All Plants Surveyed 18

2. Benzene/Toluene/Xylene Plants 22

3. Ethylene Plants 30

4. Ethylene Oxide/Ethylene Glycol Plants 36

5. Polyethylene Plants 41

6. Maleic Anhydride Plants 48

TABLE OF CONTENTS

7. Ethylbenzene/Styrene Plants 48

C. Comparison of Fugitive Emission Estimation Methods 56

D. VOC Emission Controls in Use 56

1. Process Sources 56

2. Fugitive Sources 60

3. Storage and Loading Sources 61

E. Gaps in Available Data and Methods 62

1. Process Sources 62

2. Fugitive Sources 63

3. Storage and Loading Sources 63

IV. TECHNOLOGIES/OPTIONS AVAILABLE FOR THE CONTROL OF VOC EMISSIONS 65

A. Control of Process Vent Emissions 65

1. Combustion 65

(a) Flares 65
(b) Incinerators 75

(i) Catalytic Oxidation 75
(ii) Thermal Incinerators 75

(c) Boilers/Heaters/Furnaces 81

2. Condensation 82

3. Adsorption 84

4. Absorption 88

TABLE OF CONTENTS

5. Process and Equipment Modifications 89

B. Control of Fugitive Emissions 91

1. Inspection and Repair Programs 91

2. Replacement of Leaking Equipment with Low or Non-Leaking Equipment 97

3. Capture of Emissions and Rerouting to a Control Device 99

C. Control of Emissions from the Storage of Chemicals 100

1. Fixed Roof Tanks 100

(a) Internal Floating Roofs 100
(b) Vapour Balancing Coupled with a Control Device 100

D. Control of Emissions from the Transfer of Chemicals 101

E. Socioeconomic Impacts 101

V. IMPACTS OF CONTROLS FOR SURVEYED PLANTS 103

A. Control Scenarios 103

1. Scenario 1 - Control of Process, Storage and Transfer Emissions 103

2. Scenario 2 - Control of All Emissions 106

B. Potential VOC Emission Reductions 107

1. Reductions Under Scenario 1 107

2. Reductions Under Scenario 2 107

VI. CONCLUSIONS AND RECOMMENDATIONS 112

A. Conclusions 112

B. Recommendations 115

TABLE OF CONTENTS

VII. REFERENCES 116

LIST OF APPENDICES

APPENDIX A QUESTIONNAIRE PACKAGE FOR THE SURVEY

APPENDIX B FUGITIVE EMISSION CONTROL PROGRAMS AT SEVERAL SURVEYED COMPANIES

LIST OF FIGURES

FIGURE II-1	STRATEGIES FOR ESTIMATING FUGITIVE EMISSIONS AT CHEMICAL PLANTS	12
FIGURE III-1	1988 VOC EMISSIONS BY SOURCE TYPE	19
FIGURE III-2	COMPARISON OF 1985 AND 1988 VOC EMISSIONS BY SOURCE TYPE	21
FIGURE III-3	1988 VOC EMISSIONS BY PRODUCT TYPE	24
FIGURE III-4	1988 VOC EMISSIONS FROM BENZENE, TOLUENE AND XYLENE PLANTS	26
FIGURE III-5	DISTRIBUTION OF VOC EMISSIONS BY SOURCE TYPE FOR BTX PLANTS	27
FIGURE III-6	1988 VOC EMISSIONS FROM ETHYLENE PLANTS	32
FIGURE III-7	DISTRIBUTION OF VOC EMISSIONS BY SOURCE TYPE FOR ETHYLENE PLANTS	33
FIGURE III-8	1988 VOC EMISSIONS FROM ETHYLENE OXIDE/ETHYLENE GLYCOL PLANTS	38
FIGURE III-9	DISTRIBUTION OF VOC EMISSIONS BY SOURCE TYPE FOR ETHYLENE OXIDE/ETHYLENE GLYCOL PLANTS	39
FIGURE III-10	1988 VOC EMISSIONS FROM POLYETHYLENE PLANTS	43
FIGURE III-11	DISTRIBUTION OF VOC EMISSIONS BY SOURCE TYPE FOR POLYETHYLENE PLANTS	44
FIGURE III-12	1988 VOC EMISSIONS FROM MALEIC ANHYDRIDE PLANTS (1)	50
FIGURE III-13	1988 VOC EMISSIONS FROM ETHYLBENZENE/STYRENE PLANTS	52
FIGURE III-14	DISTRIBUTION OF VOC EMISSIONS BY SOURCE TYPE FOR ETHYLBENZENE/STYRENE PLANTS	53
FIGURE III-15	COMPARISON OF FUGITIVE EMISSION ESTIMATES MADE USING ALTERNATE METHODS	58
FIGURE IV-1	DESTRUCTION EFFICIENCY OF DIFFERENT GASES	67

LIST OF FIGURES

FIGURE IV-2	COMBUSTION EFFICIENCY VS FLAME STABILITY FOR STEAM-INJECTED AND PRESSURE-ASSISTED FLARE HEADS	68
FIGURE IV-3	SCHEMATICS OF A VARIETY OF FLARE TYPES	71
FIGURE IV-4	OPERATING COSTS FOR A VARIETY OF FLARE TYPES	73
FIGURE IV-5	CAPITAL COSTS FOR A VARIETY OF FLARE TYPES	74
FIGURE IV-6	PROCESS FLOW SKETCH - CATALYTIC OXIDATION SYSTEM	76
FIGURE IV-7	PERCENT WEIGHT OF TOLUENE REMAINING AFTER THERMAL OXIDATION AT 760°C	79
FIGURE IV-8	EFFECTS OF EXCESS AIR/OXYGEN ON THERMAL DESTRUCTION OF ORGANIC COMPOUNDS (BENZENE)	80
FIGURE IV-9	TYPICAL REFRIGERATED VAPOUR-RECOVERY SYSTEM FOR A STORAGE TANK OR PRODUCT TRANSFER STATION	83
FIGURE IV-10	ADSORPTION ISOTHERMS OF HYDROCARBON VAPOURS	85
FIGURE IV-11	MOVEMENT OF VAPOUR CONCENTRATION DISTRIBUTION CURVE IN CARBON BED WITH INCREASED ADSORPTION TIME	86

LIST OF TABLES

TABLE I-1	CEPA PRIORITY SUBSTANCES LIST	2
TABLE I-2	NATIONAL VOC EMISSIONS BY MAJOR SOURCE SECTOR FOR 1985	3
TABLE II-1	FUGITIVE EMISSION SOURCES AND ALTERNATE EMISSION FACTORS	11
TABLE III-1	COMPARISON OF 1985 AND 1988 RESULTS FOR SURVEYED PLANTS	20
TABLE III-2	VOC EMISSIONS BY PRODUCT	23
TABLE III-3	BTX PLANT EMISSIONS	25
TABLE III-4	BTX PLANTS - EMISSIONS OF VOCS AND PRIORITY SUBSTANCES	28
TABLE III-5	ETHYLENE PLANT EMISSIONS	31
TABLE III-6	ETHYLENE PLANTS - EMISSIONS OF VOCS AND PRIORITY SUBSTANCES	34
TABLE III-7	ETHYLENE OXIDE/ETHYLENE GLYCOL PLANT EMISSIONS	37
TABLE III-8	ETHYLENE OXIDE/ETHYLENE GLYCOL PLANTS - EMISSIONS OF VOCs AND PRIORITY SUBSTANCES	40
TABLE III-9	POLYETHYLENE PLANT EMISSIONS	42
TABLE III-10	POLYETHYLENE - EMISSIONS OF VOCs AND PRIORITY SUBSTANCES	45
TABLE III-11	MALEIC ANHYDRIDE PLANT EMISSIONS	49
TABLE III-12	MALEIC ANHYDRIDE PLANTS EMISSIONS OF VOCS AND PRIORITY SUBSTANCES	49
TABLE III-13	ETHYLBENZENE/STYRENE PLANT EMISSIONS	51
TABLE III-14	STYRENE/ETHYLBENZENE PLANTS - EMISSIONS OF VOCS AND PRIORITY SUBSTANCES	54
TABLE III-15	COMPARISON OF FUGITIVE EMISSION ESTIMATION METHODS	57
TABLE III-16	SUMMARY OF FLARES IN USE	59

LIST OF TABLES

TABLE IV-1	SUMMARY OF FLARE TYPES	70
TABLE IV-2	THERMAL DESTRUCTION TEMPERATURES TO ACHIEVE 99% DESTRUCTION EFFICIENCY (TEMPERATURE °C)	78
TABLE IV-3	FRACTION OF TOTAL MASS EMISSIONS FROM VARIOUS SOURCE TYPES THAT WOULD BE AFFECTED BY DIFFERENT ACTION LEVELS	93
TABLE IV-4	ESTIMATED OCCURRENCE AND RECURRENCE RATE OF LEAKS FOR VARIOUS MONITORING INTERVALS	95
TABLE IV-5	AVERAGE EMISSION RATES FROM SOURCES ABOVE 10,000 PPMV AND AT 1000 PPMV	96
TABLE IV-6	EFFECTIVENESS OF EQUIPMENT MODIFICATIONS	98
TABLE V-1	SUMMARY OF CONTROLLED AND UNCONTROLLED EMISSIONS BY SOURCE AND PRODUCT TYPE	104
TABLE V-2	SUMMARY OF VOC EMISSIONS BY SOURCE TYPE AFTER SCENARIO 1 CONTROLS	105
TABLE V-3	EMISSIONS BY PRODUCT TYPE AFTER SCENARIO 1 CONTROLS	108
TABLE V-4	SUMMARY OF VOC EMISSIONS BY SOURCE TYPE AFTER SCENARIO 2 CONTROLS	109
TABLE V-5	EMISSIONS BY PRODUCT TYPE AFTER SCENARIO 2 CONTROLS	110
TABLE VI-1	EMISSIONS OF BTX AND STYRENE	113

I. INTRODUCTION

A. Background

Volatile organic compounds (VOCs) by definition are considered to include all organic compounds which participate in atmospheric photochemical reactions. The following organic compounds are designated as having negligible photochemical reactivity, and are excluded from VOCs: methane, ethane, methyl chloroform (1,1,1-trichloroethane), CFC-113 (trichlorotrifluoroethane), methylene chloride, CFC-11 (trichlorofluoromethane), CFC-12 (dichlorodifluoromethane), CFC-22 (chlorodifluoromethane), FC-23 (trifluoromethane), CFC-114 (dichlorotetrafluoroethane), CFC-115 (chloropentafluoroethane), HCFC-123 (dichlorotrifluoroethane), HFC-134a (tetrafluoroethane), HCFC-141b (dichlorofluoroethane), HCFC-142b (chlorodifluoroethane). For the purposes of this survey, the VOCs are total hydrocarbons (THC).

VOC emissions are of interest because they can react with other gases in the atmosphere, leading to the formation of ozone, and could contain some volatile organic chemicals which affect human health and the environment. The Canadian Environmental Protection Act (CEPA) includes a list of priority substances which may be deterimental to human health and the environment. Table I-1 lists the priority substances using the assigned priority groupings (1, 2 and 3).

The organic chemical industry produces a wide variety of chemicals that are used in the production of plastics, consumer products, coatings, fabrics and many other products in common use throughout Canada. These industrial plants are sources of volatile organic compounds and contribute to an as-yet poorly quantified extent to the national total. The most recent national inventory of VOC emissions, which applies to 1985 (IMD, 1989), shows transportation sources contribute the largest share, at 48.4%, followed by miscellaneous solvent use (27%), industrial processes (14.4%), fuel combustion (9.1%) and incineration (1.1%). The contributions of the major source sectors to VOC emissions in Canada are summarized in Table I-2 for reference. With the best, but limited information available for 1985, the annual emissions of VOCs from the organic chemical industry were estimated to be 107,793 tonnes, amounting to 6% of the national total. This includes emissions from process vents (assumed in the inventory to be emitting without use of control equipment), fugitive equipment leaks, and storage and handling of feed, intermediates and products. Because information was not available for the 1985 inventory on the level of control of process emissions in the organic chemical industry, the calculated emissions were considered to be in excess of actual levels.

The emission estimates included in the 1985 national inventory were based on the results of a study of VOC emissions from the organic chemical industry prepared by B.H. Levelton & Associates Ltd. (Edwards and Wilkin, 1987). VOC emissions were determined in this study using publically available data on the number, location and production capacity of plants producing organic chemicals in Canada. Estimates of emissions from process sources were made using uncontrolled emission factors for standard source categories developed by the U.S. EPA (Radian, 1987), and assuming these emissions were not reduced by any type of pollution

TABLE I-1 CEPA PRIORITY SUBSTANCES LIST

Group 1	Arsenic (7440-38-2) and its compounds
	Benzene (71-43-2)
	Effluents from pulp mills using bleaching
	Hexachlorobenzene (118-74-1)
	Methyl tertiary-butyl ether (1634-04-4)
	Polychlorinated dibenzodioxins
	Polychlorinated dibenzofurans
	Polycyclic aromatic hydrocarbons
	Waste crankcase oils
Group 2	Cadmium (7440-43-9) and its compounds
	Chlorinated waste water effluents
	Chlorobenzene (108-90-7)
	Chromium (7440-47-3) and its compounds
	Creosote-impregnated waste materials
	Dibutyl phthalate (84-74-2)
	1,2-Dichlorobenzene (95-50-1)
	1,4-Dichlorobenzene (106-46-7)
	1,2-Dichloroethane (107-06-2)
	Dichloromethane (75-09-2)
	Di-n-octyl phthalate (117-84-0)
	bis(2-Ethylhexyl) phthalate (117-81-7)
	Inorganic fluorides
	Nickel (7440-02-0) and its compounds
	Pentachlorobenzene (608-93-5)
	Styrene (100-42-5)
	Tetrachlorobenzenes
	1,1,2,2-Tetrachloroethane (79-34-5)
	Tetrachloroethylene (127-18-4)
	Toluene (108-88-3)
	Trichlorobenzenes
	1,1,1-Trichloroethane (71-55-6)
	Trichloroethylene (79-01-6)
	Xylenes (1330-20-7)
Group 3	Aniline (62-53-3)
	Benzidine (92-87-5)
	Chlorinated paraffin waxes (63449-39-8)
	bis(2-Chloroethyl) ether (111-44-4)
	bis(chloromethyl) ether (542-88-1)
	Chloromethyl methyl ether (107-30-2)
	3,3-Dichlorobenzidine (91-94-1)
	3,5-Dimethylaniline (108-69-0)
	Methyl methacrylate (80-62-6)
	Mineral fibres
	Organotin compounds (non-pesticidal uses)

TABLE I-2 NATIONAL VOC EMISSIONS BY MAJOR SOURCE SECTOR FOR 1985

SOURCE SECTOR	ANNUAL EMISSION (tonne)
Industrial	
Crude Oil	15,020
Refineries	40,164
Petrochemicals	107,793
Plastics	48,619
Kraft pulping	14,515
Other	32,172
Subtotal	258,283 (14.4%)
Fuel Combustion	
Refineries	671
Gas plants	6,301
Other industrial	42,617
Commercial	1,331
Residential	2,662
Fuel wood	107,866
Power plants	2,620
Subtotal	164,068 (9.1%)
Transportation	
Cars (gasoline and diesel)	494,105
Light duty trucks	193,171
Heavy duty trucks	63,593
Motorcycles	4,366
Other transportation	114,979
Subtotal	870,215 (48.4%)
Incineration	19,370 (1.1%)
Miscellaneous	
Fuel marketing	108,771
Slash burning	80,809
Solvent use	290,190
Other	6,262
Subtotal	486,032 (27.0%)
National Total	1,797,969

abatement equipment. The latter assumption was made because information on the pollution control equipment in use by the industry was not available on a plant specific basis. The study made estimates of fugitive emissions from leaking process equipment, such as pumps, valves, flanges and pressure relief valves, and emissions from storage tanks and product loading operations, using various factors and generalized estimating techniques. Because of the lack of data on emission controls for the study, it was recommended that a survey be conducted to obtain data on the type and efficiency of VOC controls in use by the industry and that this be used to improve the estimates of emissions from process and other sources.

This study was undertaken to develop a methodology for updating the inventory of emissions from the organic chemical industry using data provided by individual plants, to prepare an inventory of emissions from selected, larger chemical plants of particular interest because of chemicals which could potentially be emitted to the atmosphere and to determine the options for, and impacts of, VOC controls. Chapter II discusses the methodology used to obtain data and calculate emissions. A summary of emissions from the plants surveyed in the study is given in Chapter III. An overview of control options for process, fugitive, and storage and loading emission sources is given in Chapter IV in sufficient detail to support the analysis of the impacts of controls in Chapter V. The discussion of control options is not an exhaustive treatment of this complex subject, since numerous other recent studies are available. The conclusions and recommendations included in the report are oriented towards the inventory methodology and what future work is needed to improve future inventories.

B. Scope of Work

The principal objectives of this study were to prepare an inventory of VOC emissions from selected organic chemical plants, to determine the control options available to these and other plants, and to describe the impacts if control strategies were implemented. The specific objectives of the study were:

Phase I

- finalize the plants to be included in the survey in conjunction with the VOC Task Force. Plants to be included produce: polyethylene, ethylene, ethylbenzene/styrene, ethylene oxide/ethylene glycol, maleic anhydride and benzene, toluene and xylenes;

- conduct a one-day workshop to finalize the calculation methodologies and questionnaires to be used for the VOC inventory. The inventory is to include VOCs, benzene, toluene, xylenes and styrene;

- develop and finalize the questionnaires to be sent to participating plants for obtaining information on VOC emissions, control equipment and codes of practise associated with emissions;

- send out and collect the questionnaires.

Phase II

- prepare an inventory of emissions of VOCs, benzene, toluene, xylene and styrene from the plants participating in the survey;
- review VOC control technology appropriate to organic chemical plants;
- examine the impacts of implementing selected control strategies on emissions for the plants participating in the survey;
- review qualitatively the socio-economic impacts and benefits of implementation of control strategies.

II. INVENTORY METHODOLOGY

A. Types of VOC Sources

Volatile organic compounds (VOCs) are emitted from various types of sources at chemical plants. By convention, these are grouped according to the type of emission sources involved, as follows:

Process Emissions

Process emissions are those which originate from the manufacturing process and are discharged through continuous or intermittent vents, vessel openings, discharge stacks and similar equipment. These sources may emit directly to the atmosphere or may discharge to VOC control equipment which subsequently emits a reduced level of VOCs to the atmosphere. This study excluded stationary combustion sources of VOCs, such as boilers and fired heaters, which are used in the manufacturing process for space heating or power generation. VOC emissions from waste gas incinerators and flares were included.

Fugitive Emissions

Fugitive emissions refer to VOC discharges to the atmosphere which may occur at mechanical connections and sampling lines throughout a chemical plant. These are categorized as follows:

- valves
- pump seals
- compressor seals
- pressure relief valves
- flanges
- open-ended lines
- sampling connections.

Storage and Loading Sources

Storage emissions originate from storage vessels used to contain feedstocks, intermediate stocks and final products. The vessels considered in the study are fixed roof tanks, external floating roof tanks, internal floating roof tanks and horizontal tanks. Pressurized storage tanks were excluded.

Loading sources refer to emissions arising during the loading of a product into a tanker truck, rail tank car, barge or ship for shipment from the plant.

Spills

VOC emissions can occur from evaporation of volatile components of liquid spills or from gaseous releases of VOC containing streams to the atmosphere from safety pressure relief equipment or by equipment failure. Because spills are random events and their number and size varies widely from year to year, the study considered a three-year average of spills to be representative.

B. Approach to Inventory Methodology Development

Initially, the inventory of VOC emissions was to be prepared from specific data supplied to B.H. Levelton & Associates Ltd. staff by the plants participating in the survey, who would utilize some accepted methodologies to calculate VOC emissions. This and alternate approaches to calculation of emissions were discussed with representatives of Environment Canada and the Canadian Chemical Producers Association (CCPA) early in the project and it was agreed that industry personnel would calculate VOC emissions using methodologies that would be formulated during the project and would report essential data used in these calculations and the final emission results on standardized data sheets. The data used in the calculations would be provided with the final emission results to allow the response to be checked for calculation errors and to adequately document the methods and base data used.

A review of published reports was conducted in March and April, 1989, to obtain information on VOC emission calculation methodologies for the types of plants included in the survey. From the results of the review, emission factors and calculation methodologies were compiled and prepared in an appendix format suitable for distribution to participating companies. Essentially all information on VOC emissions was obtained from the U.S. EPA and the American Petroleum Institute. A very useful compilation of methods for calculating fugitive emissions was obtained from the Chemical Manufacturers Association. However, this material was largely extracted from reports issued by the U.S. EPA.

A draft questionnaire was developed for the emissions survey. It consisted of sections which contained background and instructions; data sheets; and emission factors and equations. This document was reviewed in detail at a workshop held on May 2, 1989 by the Environment Canada/CCPA VOC Task Force to identify areas needing clarification, revision and improvement. The questionnaire was subsequently revised and distributed to participating companies for use in calculating emissions. Subsequent to this, some clarification of the waste water streams included in the study and corrections or clarifications to the emission calculation methodologies were made and distributed to participating companies.

The final version of the questionnaire is included in Appendix A for reference or for use in any future inventory that may be undertaken. This version incorporates the changes noted above.

The following sections elaborate on the methodologies used for each major source type and provide the rationale for the selection of the methodology adopted for this survey.

C. Process Sources

Process sources refer to continuous or intermittent discharges of VOCs to the atmosphere which occur as an inherent feature of the process equipment or plant design. This includes for example, continuous and intermittent vents for process vessels, analyzer vents, purging of vessels, as well as flares. The quantity emitted is the amount that enters the atmosphere, either directly or downstream of appropriate control equipment, such as an absorbtion system, incinerator or flare.

Process sources include those within the battery limits of the specific production plant and exclude stationary combustion sources, except for any VOC emissions resulting from incineration of waste gas streams where the primary purpose is destruction of VOCs before release to the atmosphere. VOCs emitted by process heaters and boilers fired with fuel gases from the plant were not included in survey, though some plants reported these emissions in the interest of completeness. Cooling towers were included as a secondary emissions source if fed VOC containing water streams. VOC emissions for waste water were considered as secondary emissions and were included when within the battery limits of the production unit.

Emissions from process sources were calculated using one of two methods. The preferred method was to calculate emissions using measured data for the flow rate, hours of operation, and composition of the discharged steam using an equation of the general form:

$$\textit{VOC Emission (kg)} = A \times B \times C \times \frac{(100 - D)}{100} \times \frac{kg}{1000g}$$

where

A = volume flowrate, m^3/h
B = hours of operation (h/year)
C = VOC concentration (g/m^3)
D = VOC removal efficiency of control equipment (%)

If measured data was not available for flowrate or VOC concentration, engineering estimates were to be made by plant personnel from knowledge of production rates, design specifications or comparable information, and noted accordingly in the data sheets.

The second method that could be used for emissions relies on empirically derived emission factors, which are a ratio of the uncontrolled VOC emission to the annual amount of

an associated base quantity, for example, annual styrene production. The estimate derived in this manner is then adjusted to reflect the effect of control equipment as follows:

$$\text{VOC Emission (kg)} = A \times B \times \frac{(100 - C)}{100}$$

where

A = base quantity (tonnes/yr)
B = uncontrolled emission factor (kg/tonne)
C = VOC removal efficiency of control equipment (%)

Other units may be used to express the base quantity and the emission factor as long as the units are consistent.

Emission factors were extracted from U.S. EPA reports for the types of plants and processes included in the survey. Emission factors have not been developed for all sources present at the plants surveyed, and often apply to processes and plant designs that differ from what is in use in Canada. Plant respondents were asked to exercise discretion when selecting and applying the published emission factors to ensure the calculated emission realistically represented actual conditions.

The control efficiencies to be used to calculate annual VOC emissions, either by measured data or emission factors, is the annual average value, inclusive of the effects of upsets in operation, down time or other factors. The VOC removal efficiency for the control equipment is the ratio of the VOC removed to the VOC input, expressed as a percentage. Descriptive information was requested from surveyed plants for each VOC control system, and included a description of the system and its operation, the control efficiency and the source of this data, as well as a discussion of the factors that affect the unit's annual effective efficiency.

Emissions of chemicals on the CEPA Priority Substances List (PSL) were included in the inventory. The principal PSL chemicals for the plants selected for the survey are benzene, toluene, xylenes and styrene. Respondents were to determine the weight fraction of these that are present for each process source. Preferably, this data was to be determined by measurement, but where this type of data was not available, estimates by other means were to be provided, with a supporting explanation. The efficiency of removal for PSL chemicals was to be provided if available, though this was seldom the case of the plants surveyed. Consequently, the removal efficiency for PSL chemicals was taken to be the same as for VOCs as a whole when more specific data was not provided.

D. Fugitive Sources

Fugitive emissions arise from leaks at mechanical connections and from open sampling systems which discharge some small amount of VOC containing streams to the atmosphere. Emissions were calculated for the fugitive sources and services listed in Table II-1, which have evolved from a number of studies of the organic chemical industry and petroleum refining industry for the U.S. EPA.

Fugitive emissions can be calculated using one or more of the following available methods, which yield emission estimates of increasing accuracy:

I Average SOCMI (Synthetic Organic Chemical Manufacturing Industry) emission factors

II Leak/No-leak emission factors

III Stratified emission factors

IV Stratified emission statistics for equipment, with emission factor correlation equations.

V Unit-specific correlations by bagging of equipment

The strategies for determining fugitive emissions are illustrated schematically in Figure II-1, which also shows the increasing data requirements and analysis required for each method.

At a minimum, plants were to use Method I with counts of equipment from process and instrumentation drawings, supplementing this data with field verification as appropriate and when possible. Other fugitive emission calculation methods could be used to improve on the estimate of emission from these sources determined by Method I. The choice of advanced method and the extent of any field work for counting and screening equipment was left to plant personnel. A limited number of plants surveyed used Method II, III and IV techniques and reported these results along with results from Method I. Emission factors for Methods I, II and III are summarized in Table II-1. The questionnaire package included factors for Methods I and II. Data for use of the more detailed methods were available to the surveyed plants from the manual prepared by the Chemical Manufacturers's Association (CMA, 1989).

Annual fugitive emissions were calculated using the equation:

$$\textit{Fugitive Emission (kg)} = A \times B \times C$$

where

A = count of equipment for standard type and service
B = emission factor for equipment
C = hours of operation

TABLE II-1 FUGITIVE EMISSION SOURCES AND ALTERNATE EMISSION FACTORS

Equipment	Service[a]	Average SOCMI kg/source/h	Leak - No-Leak		Stratified Screening values, ppmv		
			Leaking[b]	Non-leaking[b]	0 - 1,000	1,001 - 10,000	>10,000
			kg/source/h		kg/source/h		
Valves	Gas/vapour	0.0056	0.0451	0.00048	0.00014	0.00165	0.0451
	Light liquid	0.0071	0.0852	0.00171	0.00028	0.00963	0.0852
	Heavy liquid	0.00023	0.00023	0.00023	0.00023	0.00023	0.00023
Pump Seals	Light liquid	0.0494	0.437	0.0120	0.00198	0.0335	0.437
	Heavy liquid	0.0214	0.3885	0.0135	0.00380	0.0926	0.3885
Compressor Seals	Gas/vapour	0.228	1.608	0.0894	0.01132	0.264	1.608
pressure relief valve	Gas/vapour	0.104	1.691	0.0447	0.0114	0.279	1.691
Flanges	All	0.00083	0.0375	0.00006	0.00002	0.00875	0.0375
Open-ended lines	All	0.0017	0.01195	0.00150	0.00013	0.00876	0.01195
Sampling connections	All	0.0150	Same as SOCMI		Same as SOCMI		

[a] Definitions of service types are included in the "Background and Instructions" section of the questionnaire (Appendix A)

[b] Leaking - ≥10,000 ppm concentration; Non-leaking - <10,000 ppm concentration; based on screening survey

Source: CMA, 1989

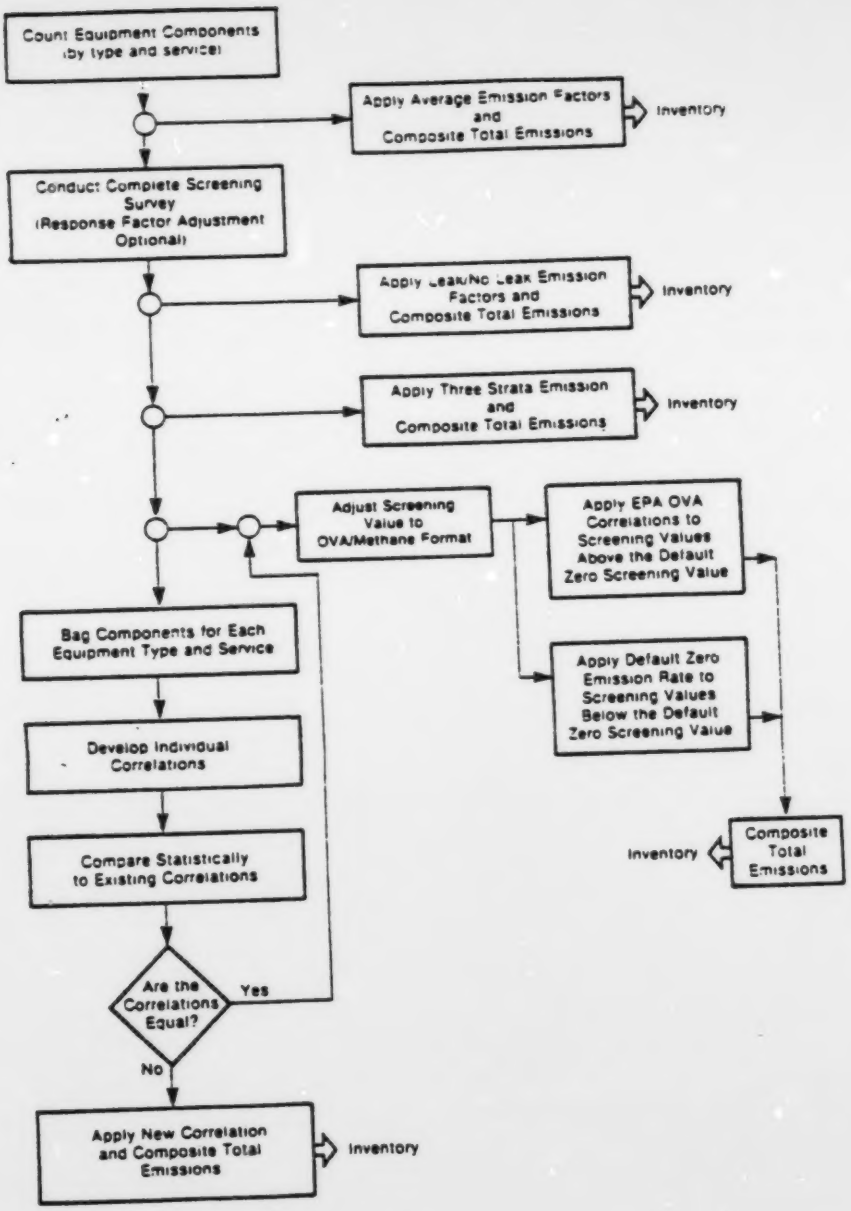

Count Equipment Components (by type and service)
Apply Average Emission Factors and Composite Total Emissions
Inventory
Conduct Complete Screening Survey (Response Factor Adjustment Optional)
Apply Leak/No Leak Emission Factors and Composite Total Emissions
Inventory
Apply Three Strata Emission and Composite Total Emissions
Inventory
Adjust Screening Value to OVA/Methane Format
Apply EPA OVA Correlations to Screening Values Above the Default Zero Screening Value
Apply Default Zero Emission Rate to Screening Values Below the Default Zero Screening Value
Inventory
Composite Total Emissions
Bag Components for Each Equipment Type and Service
Develop Individual Correlations
Compare Statistically to Existing Correlations
Are the Correlations Equal?
Yes
No
Apply New Correlation and Composite Total Emissions
Inventory

FIGURE II-1 STRATEGIES FOR ESTIMATING FUGITIVE EMISSIONS AT CHEMICAL PLANTS

Source: CMA, 1989

If VOC control equipment was used to reduce emissions from certain types of fugitive sources, the uncontrolled annual emission calculated using the equation above was to be multiplied by (100-D)/100) where D is the VOC removal efficiency in percent.

Method I is the least rigorous method of calculating fugitive emissions in that it relies on industry average emission factors for equipment. It requires a count of the number of each of the identified fugitive sources (valves, pumps, etc), though these do not have to be sampled in the field to determine whether they are leaking, as required in the more sophisticated methods. The industry average emission factors for fugitive sources were developed from a study of 24 individual chemical process units (Radian, 1980) in the United States representing a cross section of the industry and a six-unit maintenance study (Radian, 1981). Because of their general nature, SOCMI factors may yield estimates of emissions from fugitive sources that differ markedly from actual emissions. More accurate estimates of fugitive emissions are obtained using the other available methods, with the most accurate being determined by bagging equipment and determining unit-specific emission factors (Method V).

Method II, commonly referred to as the leak/no-leak method, yields an improved estimate compared to Method I. This method requires testing of equipment in the plant with a portable analyzer to determine the number of components which have a concentration at the component of greater than or equal to 10,000 ppmv (leak) and the number of components that have a concentration of less than 10,000 ppmv (non-leaking). The resulting equipment counts are multiplied by the corresponding emission factor (Table II-1 previous) and the hours of operation to calculate emissions.

The stratified method (III) is a refinement of the leak/no-leak method. In this case the equipment is split into three populations having the following screening concentrations measured by a portable analyzer: 0 - 1,000 ppmv; 1,001 - 10,000 ppmv; and greater than 10,000 ppmv. This method requires a complete screening survey of non-hazardous equipment. From the equipment counts, the total emissions are calculated in the same way as in the methods previously discussed.

In Method IV, correlations are used to improve upon the results achieved with the stratified approach used in Method III. Concentration measurements from a survey of plant equipment with a portable analyzer can be used with correlations for valves, flanges and pump seals in a limited number of service categories developed by the U.S. EPA to yield improved emission factors compared to the three levels used in the conventional stratified method. For concentrations below the detection limit of the analyzer (0-8 ppm concentration), default zero emission factors have been developed by the U.S. EPA and need to be applied to the results from the corresponding plant equipment count. Default zero factors were determined from a relatively small population and are of dubious accuracy for general use.

Method V yields the most accurate results, but places the highest demand on resources because of the requirement to screen plant equipment with a portable analyzer and then bag selected equipment to measure the actual leak rate. Correlations must be developed relating the screening concentration to the leak rate found from bagging of components. Once the

correlations have been tested rigorously against available results and found to be superior, they can be applied to determine emissions from the plant using statistical techniques.

Fugitive emissions were calculated for all equipment components in the battery limits of the production unit for all streams containing 10%, or more volatile organic compounds. Valves less than 13 mm (1/2 inch) were excluded for the equipment counts. Standby pumps, compressors and other equipment were included if kept at operating pressure. Streams containing heat transfer fluids and heavy tars were excluded, while inclusion of all other streams was based on the service categories as defined in the questionnaire package. Equipment counts and calculated emissions were to be reported by major process section in the plant using the data sheet provided and in accordance with the process sections indicated on a simplified process block diagram provided by the plant. In all but a few cases, fugitive emissions were reported only for the plant as a whole, and not separately by major process unit.

Representative weight percentages of PSL chemicals present in the emissions from each type of fugitive source were to be reported for each major process unit and the plant overall. The principal chemicals were benzene, toluene, xylenes and styrene, for process and other emission sources. Determination of weight fractions for fugitive emissions is extremely difficult because of the number of different process streams involved and the size of the plants, especially if it is to be done for each major process section. To simplify the task, the weight fraction of PSL chemicals in the fugitive emissions were to be determined for each source type as the average of all inlet and outlet streams for each major process section. Plant personnel in most cases utilized their own knowledge of the plant, of the process and of fugitive emissions at the plant to derive representative composition data for fugitive emissions from the plant.

Plant personnel were requested to describe the codes of practise used to minimize fugitive emissions. This information was to include leak detection and repair programs, design specifications used for new facilities that were selected to yield lower fugitive emissions, or other actions taken.

E. Storage and Loading Sources

VOC emissions arise from storage tanks of various designs for feedstocks, intermediates and final products. Most tanks emit directly to the atmosphere, while for liquids having elevated vapour pressures, some tanks vent to control equipment to remove and recycle the VOC before venting to the atmosphere. The survey included the following types of tanks:

- Fixed roof
- External floating roof
- Internal floating roof
- Horizontal above-ground tanks (fixed roof)
- Caverns for ethylene storage

Pressurized bullet and spherical tanks for storage of butane, propane or other liquid under pressure were excluded from the survey because emissions from these tanks are normally near zero. Caverns are used at one plant for storage of ethylene and personnel at this plant determined the emissions using their own methods. The VOC emission characteristics of caverns are not comparable to those for conventional storage tanks.

VOC emissions were calculated using correlations developed by the American Petroleum Institute (API, 1962; API, 1983; API, 1989) as adapted by the U.S. EPA for this purpose (EPA, 1985). The reader should refer to the original documents for complete discussions of the estimation methods, the input data and the limitations of the correlations. The VOC estimation equations and input parameters for common tank types, stocks and climatic conditions are included in the questionnaire package (Appendix A). The equations given in the questionnaire package are metric versions of the original equations. The unit conversion factor is the first constant in each equation, preserving the appearance and the constants present in the original form of the equation.

The original correlations developed by the API for each type of above-ground tank are appropriate for stocks having a true vapour pressure of 10 kPa to 101 kPa, tanks vented freely to the atmosphere (no pressure/vacuum vents) and, for external floating roof tanks, average wind speeds of 3 to 24 km/h and tank diameters of 6 m or greater. In spite of the suggested restrictions on their use, the API correlations were applied to all tankage at plants in the survey. The principal problem with this approach in that many of the stored organic liquids have true vapour pressures less than the lower limit of 10 kPa, though the effect of this on the accuracy of the estimated annual emission is unknown. The significance of this and other limitations of the available emission correlations on the overall estimate of VOC emissions from the surveyed plants is expected to be negligible because of the comparatively small contribution of storage emissions to total emissions.

All tank emission calculations were done using annual statistics for the weather parameters, diurnal variation, ambient temperature and wind speed. No attempt was made in this survey to report the monthly variation of emissions that arise with changes in ambient conditions and varying tankage throughput.

The available correlations for emissions from tanks do not fully apply to all the circumstances found in the plants surveyed, which include:

- use of pressure/vacuum vents on some fixed roof tanks
- blanketed tanks (i.e. with nitrogen)
- insulated fixed roof tanks
- tanks for which the liquid level is essentially static for prolonged periods.

Tanks with high pressure vacuum vents were considered to have zero breathing loss. Emissions from the few blanketed tanks in the survey were estimated by plant personnel using measured

data. Emissions from insulated tanks were determined with the available correlations using estimates of diurnal temperature variation made by plant personnel. For tanks with static liquid levels, the throughput used for calculation of emissions was the net amount that results in changes in the liquid level.

The weight fraction of BTX and styrene in the emissions from tanks was estimated by plant personnel based on stock composition. Many of the tanks store pure stocks and the composition of the VOC emitted can be readily specified.

VOC emissions were determined for hydrocarbon product/raw material loading operations using correlations developed by the U.S. EPA (EPA, 1985). Sources included in these estimates were tanker trucks and rail tankcars. Since a reliable correlation for VOC emissions from loading of marine vessels (barges and ships) was not available, respondents were requested to provide data on the product type, the volume loaded and the loading methods, but emissions were not quantified. The methodology available from the U.S. EPA utilizes emission factors and is based on studies of emissions from marine terminals located on the Gulf of Mexico loading gasoline and crude oil. Past attempts to correlate VOC emissions from barges and ships with loading conditions, temperature, product characteristics and other parameters have been unsuccessful (Edwards and Levelton, 1987). The available emission factors for marine loading of organic liquids were felt to be inappropriate for use in this study because of differences in climate and products loaded. Sufficient data was provided for the very small number loading marine vessels for VOC emission estimates to be made at some later date if an acceptable correlation should become available.

VOC emissions from product loading were done with allowance for the VOC reduction achieved by any pollution control equipment used on this source. The annual average VOC removal efficiency of the control equipment was to be provided for each of the sources listed in the returned data sheets. The emission correlations and data sheets for loading operations are included in Appendix A.

F. Spills and Accidental Discharges to the Atmosphere

VOC emissions to the atmosphere occur from pressure relief valves, rupture disks, liquid spills and other sources of accidental discharges. These occur unpredictably and vary from year to year. Plant personnel were requested to estimate VOC emissions from spills using data on quantity discharged, composition, amount recovered, and other details available to them. In the case of liquid spills, all unrecovered volatile organics were assumed emitted to the atmosphere, where not obviously destroyed by some means or actions taken at the plant.

The reported VOC emissions from spills were the average of three years ending in 1988. A detailed list of spills was to be reported, giving information on the spill source, data, duration, VOC emitted and weight percent BTX and styrene present in the VOC released to the atmosphere. The spills to be included in the survey are the same as those normally reported to provincial government agencies.

III. EMISSIONS OF VOLATILE ORGANIC COMPOUNDS

A. Plants Included in the Inventory

The following plants were selected by Environment Canada as participants in the inventory of VOC and priority substance emissions:

Benzene/Toluene/Xylene

- Carbochem Inc., Hamilton, Ontario
- Esso Chemical Canada, Sarnia, Ontario
- Suncor Inc., Sarnia, Ontario

Ethylene

- Esso Chemical Canada, Sarnia, Ontario
- Novacor Chemicals Ltd. (Ethylene I Plant), Joffre, Alberta
- Novacor Chemicals Ltd. (Ethylene II Plant), Joffre, Alberta
- Petromont Inc., Varennes, Quebec

Ethylene Oxide/Ethylene Glycol

- Dow Chemical Canada Inc., Fort Saskatchewan, Alberta
- Union Carbide Canada Ltd., Montreal-East, Quebec
- Union Carbide Canada Ltd., Prentiss, Alberta

Polyethylene

- Dow Chemical Canada Inc., Fort Saskatchewan, Alberta (linear low density)
- Dow Chemical Canada Inc., Sarnia, Ontario (low density)
- Dow Chemical Canada Inc., Sarnia, Ontario (high density)
- Dupont Canada Inc., Corunna, Ontario (linear low density)
- Esso Chemical Canada, Sarnia, Ontario (linear low density)
- Novacor Chemicals Ltd., Joffre, Alberta (linear low density)
- Novacor Chemicals Ltd., Moore Township, Ontario (high density and low density)

Maleic Anhydride

- Monsanto Canada Inc., LaSalle, Quebec

Ethylbenzene/Styrene

- Dow Chemical Canada Inc., Sarnia, Ontario
- Polysar Ltd., Sarnia, Ontario
- Shell Canada Ltd., Scotford, Alberta

B. Emissions by Product and Source Type

1. All Plants Surveyed

The data base inventory includes data for 14 plant sites across Canada. Each plant site may contain one or more distinct process units, resulting in 21 production units being included in the survey.

The total VOC emissions from the selected plants were 10,143 tonnes in 1988. As shown in Figure III-1, emissions from process sources contribute 53% of the total, followed by fugitive emissions at 41%, storage and loading at 5%, and spills at 0.6%.

The VOC inventory conducted using 1985 data (Edwards and Wilkin, 1988) reported national VOC emissions of 110,823 tonnes from the Canadian organic chemical manufacturing industry as a whole. As a proper basis of comparison, the VOC emissions from the plants participating in this study were reported as 53,396 t in the 1985 study, compared to 10,187 t in this study. A breakdown comparing the two studies is shown in Table III-1 and Figure III-2. It should be noted that the Monsanto maleic anhydride unit was not included in the earlier study, however, its contribution (89.2 t) represents less than 1% of the 1988 total.

The most significant difference between the two sets of data is in the process emission estimates, with the 1988 process total being about 10% of the 1985 value. This difference can be attributed to the difference in calculation methodology. In the 1985 study process emissions were calculated using base quantities multiplied by uncontrolled emission factors and assuming no VOC control equipment was used. The 1988 data was supplied by the individual plants, who used combinations of emission factors, measured emissions (source testing data), mass balance calculations and engineering estimates. Furthermore, the 1988 emissions data incorporates the effect of VOC control equipment; calculated emissions are multiplied by a control efficiency where applicable, typically of the order of 95% or greater. As a result, the reported process emissions are substantially lower than those reported in the 1985 study.

The 1985 data used general EPA fugitive emission factors specified for the process and plant type. The 1988 data also used emission factors, but a more sophisticated approach was used; counts of equipment (valves, flanges, pump seals, compressor seals, pressure relief devices, open-ended lines and sampling connections) were obtained, along with the annual hours in service for each. These base quantities were then multiplied by

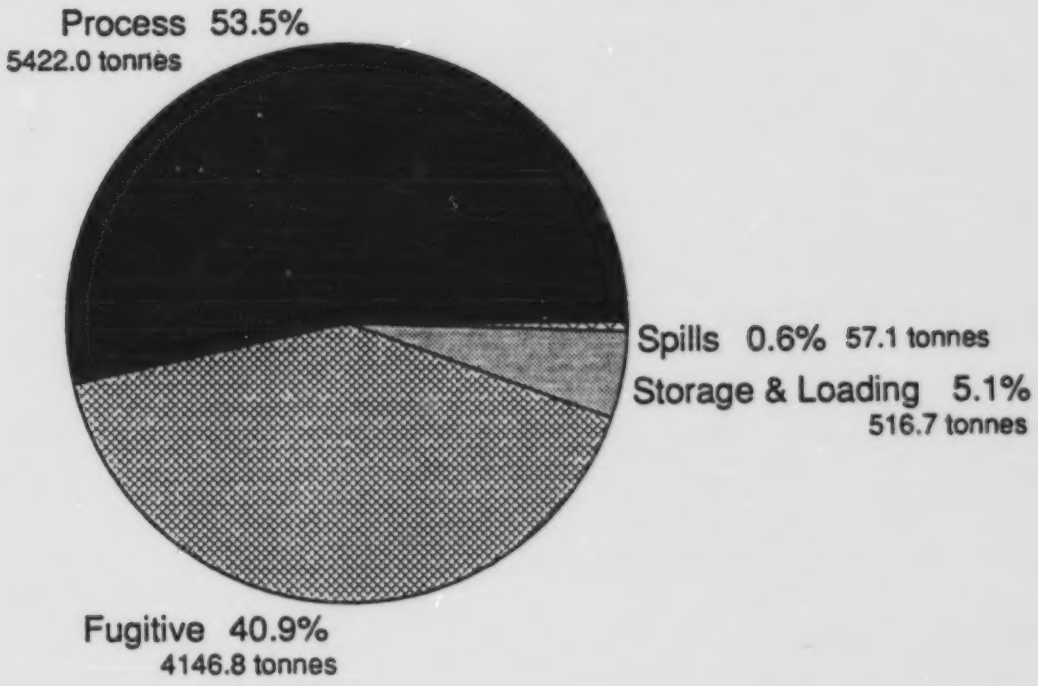


FIGURE III-1 1988 VOC EMISSIONS BY SOURCE TYPE

TABLE III-1 COMPARISON OF 1985 AND 1988 RESULTS FOR SURVEYED PLANTS

	VOC EMISSIONS (tonnes)		
	1985 DATA[a]	1988 DATA	1988/1985
Process	50,825	5,422	0.11
Fugitive	2,359	4,147	1.76
Storage and Loading	212	517	2.44
Spills	0	57	–
Total	53,396	10,143	0.19

[a] Edwards and Wilkin, 1988

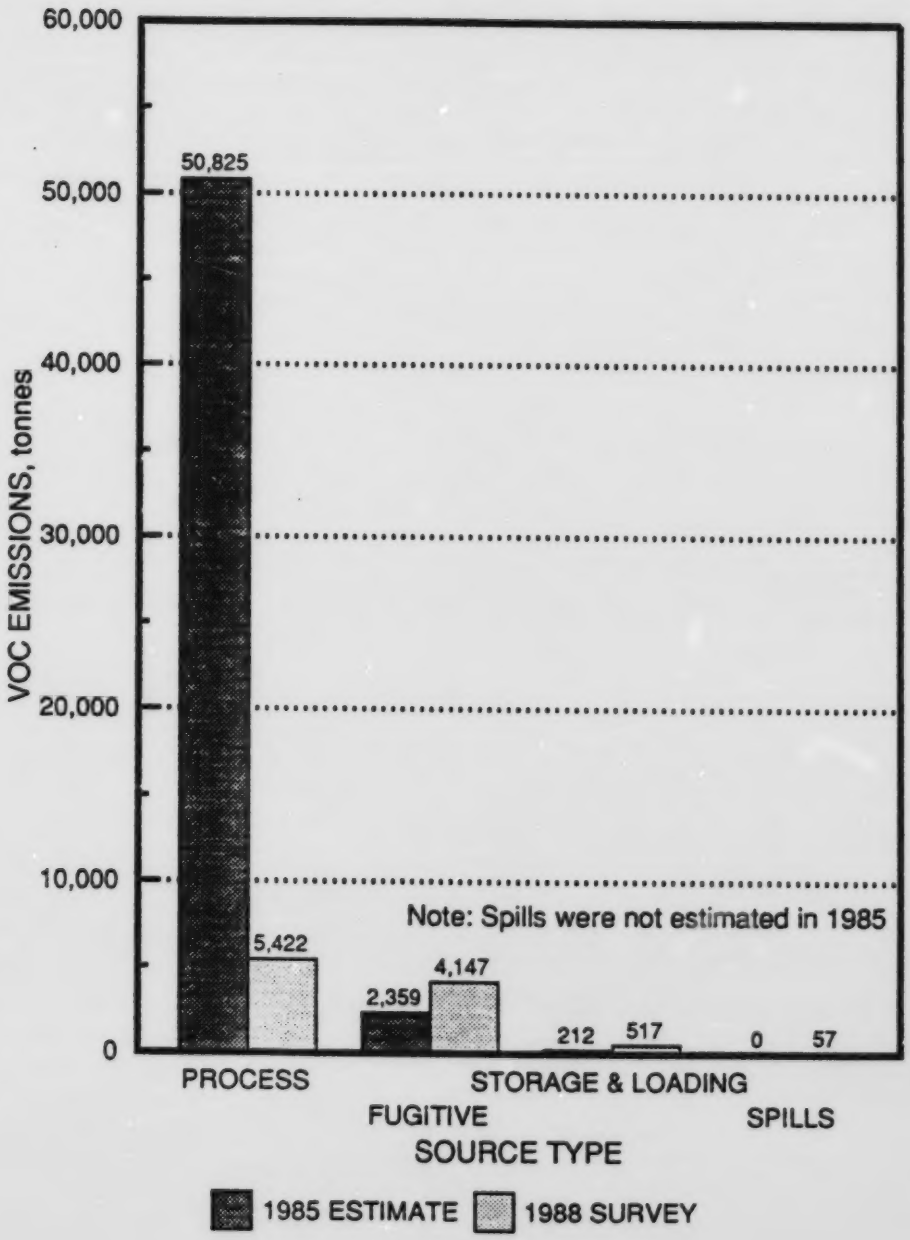


FIGURE III-2 COMPARISON OF 1985 AND 1988 VOC EMISSIONS BY SOURCE TYPE

emission factors for each equipment type. As the results show, this approach yielded a higher fugitive VOC emission total than the previous study.

Storage and loading emissions for 1988 were calculated using correlations available from the U.S. EPA (1985), with detailed data on each tank and for loading from each plant, although in some cases source measurements were made. Estimates of emissions in 1985 were developed using generalized emission factors for storage and loading and simple estimates of the volume and type of tankage used at the plants in the inventory. The methodology used for the 1988 inventory is far more accurate than that used for 1985. Estimates of spills were not made in 1985.

The breakdown of VOC emissions by chemical product is shown in Table III-2. The percent contribution of each chemical product to the total for the selected plants is shown in Figure III-3. Polyethylene plants (seven production units) contributed 41.2% of the total VOC emissions from the surveyed plants, followed by ethylene, 37.1%; ethylene oxide/ethylene glycol, 9.6%; ethylbenzene/styrene, 7.3%; benzene, toluene, xylenes, 3.97%; and maleic anhydride, 0.9%.

2. Benzene/Toluene/Xylene Plants

The benzene/toluene/xylene plant VOC emissions are shown in Table III-3, and graphed in Figures III-4 and III-5.

Table III-4 breaks down the total VOC emissions into priority substance list chemicals.

Carbochem

The Carbochem plant in Hamilton is a coal tar distillation unit, which produces heavy aromatics, pitch and oils. Process emissions for both continuous and intermittent sources were calculated using specific source data. Three pieces of control equipment were in place:

- a fired heater which incinerates vapours from the vacuum unit of each distillation unit (VOC control efficiency = 97%);
- a fume incineration system which incinerates vapours from naphthalene, heavy aromatics and oils storage (VOC control efficiency = 97%);
- a fume scrubber which scrubs vapours from pitch storage tanks (VOC control efficiency = 65%).

Fugitive emissions were calculated using Method I and were broken down by plant section (dehydrator, distillation column, storage sections).

TABLE III-2 VOC EMISSIONS BY PRODUCT

CHEMICAL PRODUCT	NUMBER OF PRODUCTION UNITS	VOC EMISSION (tonnes)				
		TOTAL	PROCESS	FUGITIVE	STORAGE & LOADING	SPILLS
Polyethylene	7	4178.3	2296.4	1761.3	120.0	0.5
Ethylene	4	3767.8	1913.6	1751.7	53.8	48.7
Ethylene Oxide/Ethylene Glycol	3	976.0	813.5	160.9	1.1	0.5
Ethylbenzene/Styrene	3	738.5	282.4	254.6	159.7	5.8
Benzene/Toluene/Xylenes	3	393.1	39.3	210.8	141.6	1.5
Maleic Anhydride	1	89.2	77.1	7.5	4.6	0.0

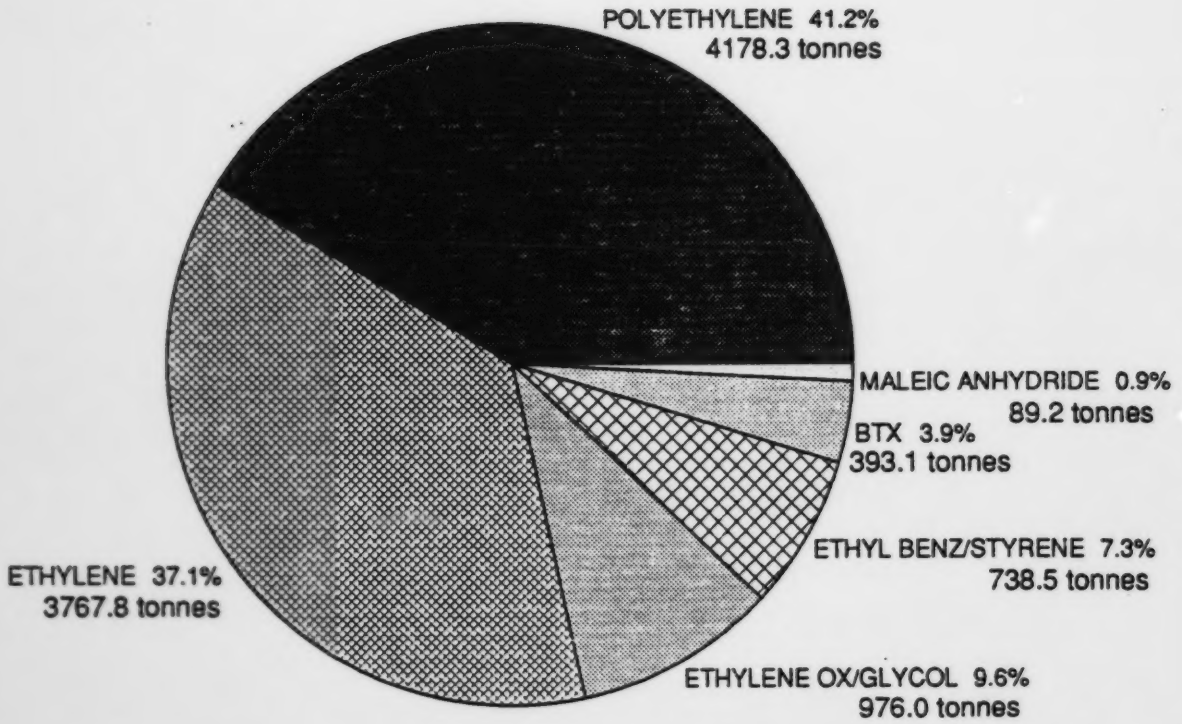


FIGURE III-3 1988 VOC EMISSIONS BY PRODUCT TYPE

TABLE III-3 BTX PLANT EMISSIONS

PLANT		NAME PLATE PRODUCTION CAPACITY	PROCESS	FUGITIVE	STORAGE & LOADING	SPILLS	PLANT TOTAL
Carbochem Inc.	t/yr	220,000	14.2	0.9	39.7	0.0	54.7
Hamilton, Ontario	%		25.9	1.6	72.5	0.0	100.0
Esso Chemical	t/yr	170,000	25.1	130.3	42.1	1.0	198.5
Sarnia, Ontario	%		12.7	65.6	21.2	0.5	100.0
Suncor	t/yr	not given	0.0	79.7	59.8	0.4	139.9
Sarnia, Ontario	%		0.0	57.0	42.7	0.3	100.0
Total BTX	t/yr		39.3	210.8	141.6	1.5	393.1
	%		10.0	53.6	36.0	0.4	100.0

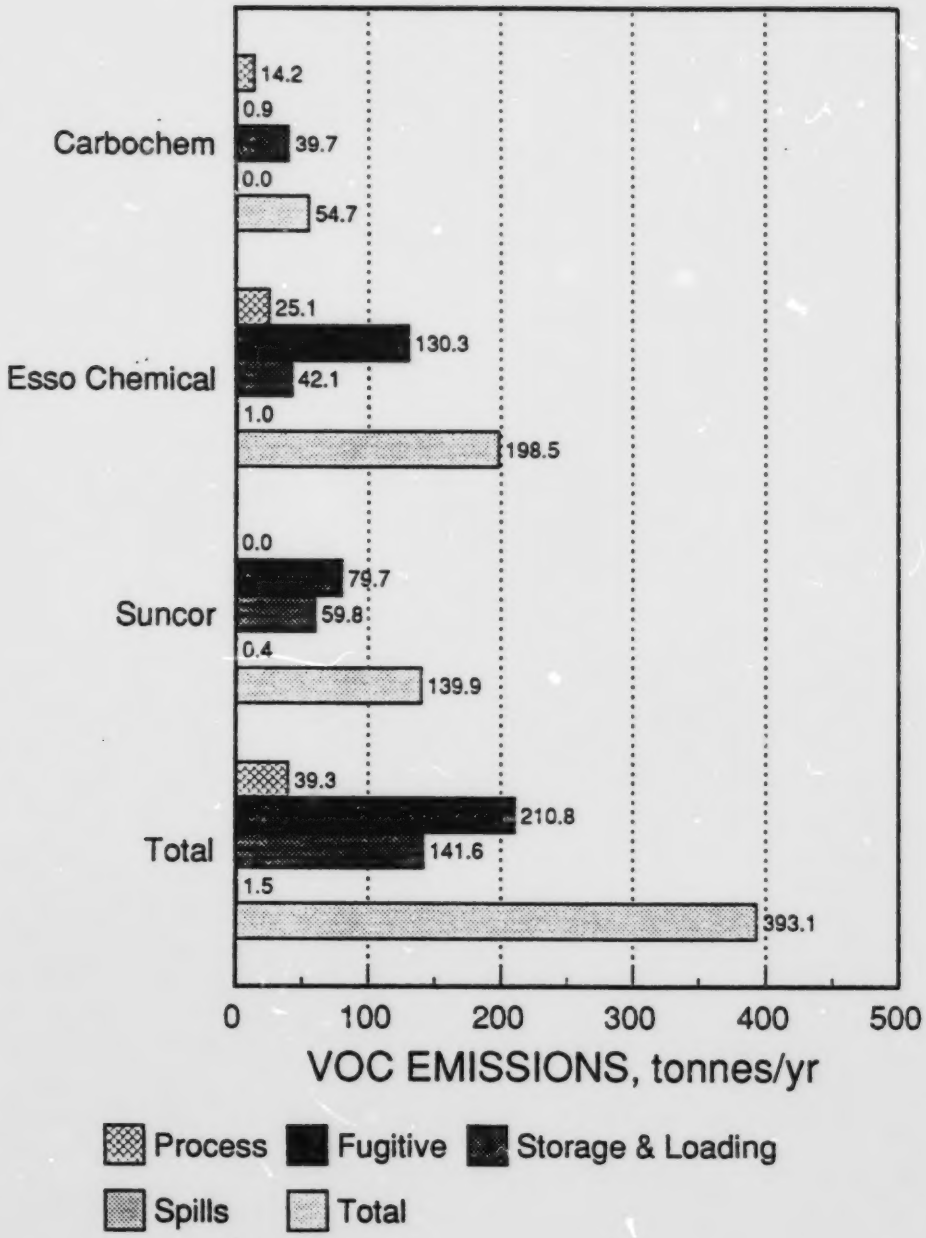


FIGURE III-4 1988 VOC EMISSIONS FROM BENZENE, TOLUENE AND XYLENE PLANTS

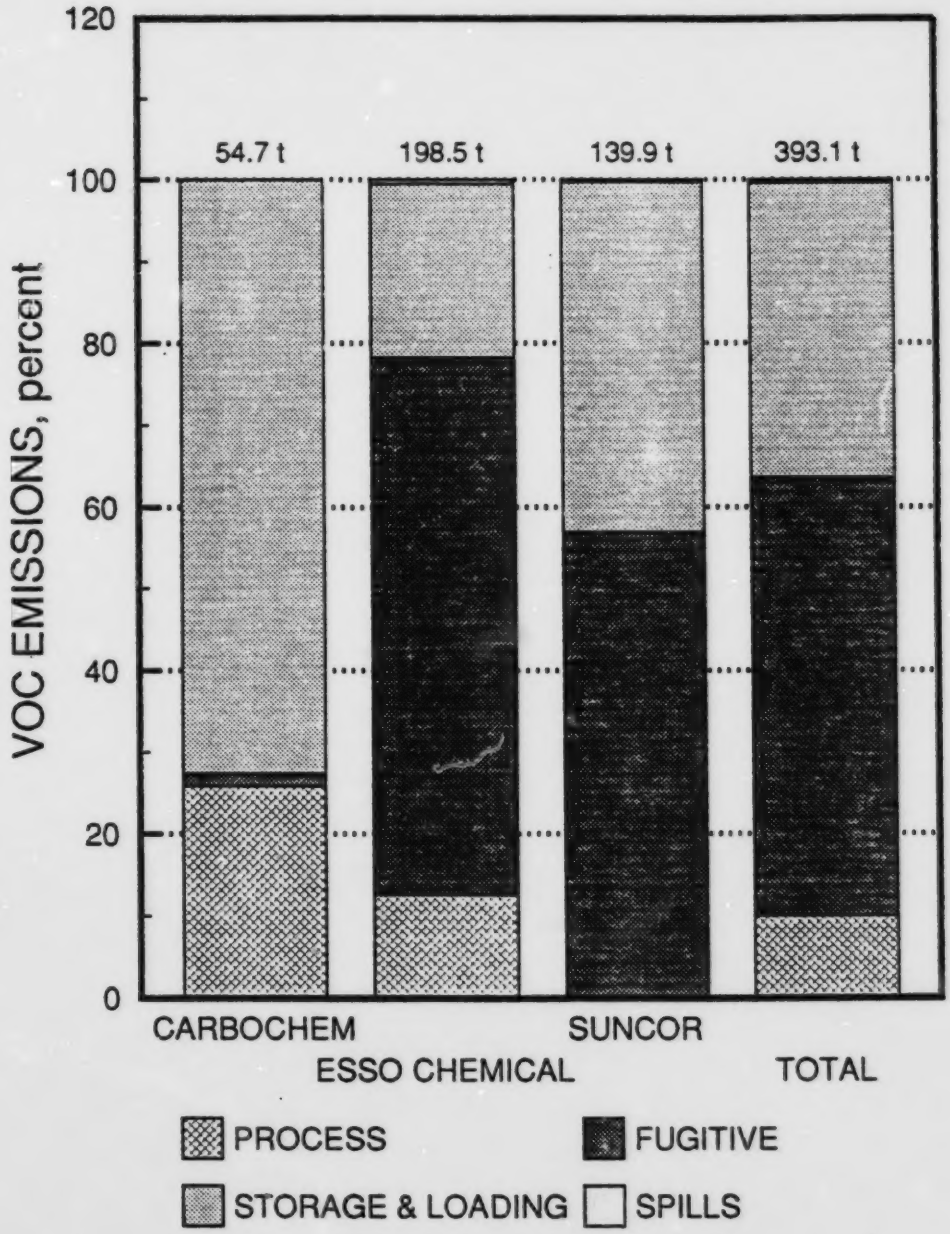


FIGURE III-5 DISTRIBUTION OF VOC EMISSIONS BY SOURCE TYPE FOR BTX PLANTS

TABLE III-4 BTX PLANTS - EMISSIONS OF VOCS AND PRIORITY SUBSTANCES

PLANT		VOC	BENZENE	TOLUENE	XYLENES	OTHER
Carbochem	t	54.7	9.9	2.9	2.9	38.0[a]
	%		18.4	5.4	5.4	70.8
Esso, Sarnia	t	198.5	63.4	25.5	25.1	84.5[b]
	%		31.9	12.8	12.6	42.6
Suncor	t	139.9	18.6	54.0	48.3	19.1[c]
	%		13.3	38.6	34.5	13.6
Total, BTX Plants	t	393.1	91.9	82.4	76.3	141.6
	%		23.4	21.0	19.4	36.0

[a] Includes pitch, aromatic oil, coal tar

[b] Includes naphthas, heavy aromatics and ethylene

[c] Composition of "other" not given

Emissions from storage tanks were calculated allowing for VOC removal efficiencies of 97% or 65%. For loading operations, a 65% VOC removal efficiency for the fume scrubber was applied.

Esso Chemical Canada, Sarnia Aromatics Recovery Unit

Esso's aromatics recovery (ARIS) unit is contained within its Sarnia refinery operation. Here, reformate is fractionated into benzene, toluene, xylenes and heavy aromatics. Emission totals include the ARIS unit itself, as well as those portions of the chemical off-sites section which are used for aromatics recovery. Process emissions were calculated using specific source data, and originate from process vents and sumps. The control equipment in place includes:

- a benzene tower overhead vent condensor, which condenses and refluxes overhead vapours from the benzene tower. The efficiency of this unit was unknown, but all source measurements were made downstream of it;

- a process flare, which flares vapours captured from process and equipment vents by a closed blowdown system (VOC control efficiency = 98%).

Fugitive emissions were estimated using the CMA/EPA average curve methodology for the ARIS unit, and with leak/no leak factors for the off-sites section. Emissions from tanks and loading operations were calculated using U.S. EPA methodologies and no recovery efficiencies were applied.

Suncor

The Suncor Sarnia refinery contains an aromatics recovery unit which separates benzene, toluene, xylenes and other heavy aromatics. The Sarnia refinery reports no process emissions for 1988, due to a closed system with no losses. No specific control system is in place, other than the venting of safety valves to flare. The bulk of the VOC emissions are from fugitive sources, and these were calculated by plant section using SOCMI factors. Emissions from tankage and loading were estimated using U.S. EPA calculation methodologies, with no recovery efficiencies applied. Fixed roof tanks were equipped with conservation vents.

BTX Plants - Comparison

For the selected BTX plants in general, process emissions are small, each being less than 30% of the plant total. Suncor has reported no process emissions. The Suncor and Esso processes are somewhat comparable, since both fractionate the refinery reformate stream, whereas the Carbochem process uses coal tar as its feedstock. The levels of emission control used at the respective plants vary, contributing to the difference in magnitude of the process emissions.

Fugitive emissions for Carbochem are much lower than that reported for Esso or Suncor. This is due to both plant size and process, and fugitive emission estimation method.

3. Ethylene Plants

VOC emissions from the selected ethylene plants are shown in Table III-5 and graphed in Figures III-6 and III-7.

Table III-6 shows the breakdown of VOC emissions into priority substance list chemicals.

Esso Chemical Canada, Sarnia, Gas Cracking Unit

Esso's Sarnia GCIS unit is designed to crack ethane, propane and butane and process it with other refinery streams to make ethylene. Emission totals include the GCIS unit itself and relevant sections of the refinery off-sites section. Process emissions were measured, and originate from process vents, analyzer vents and two flare stacks. A number of process vents were yet to be tested at the time of this report. The control equipment in place included:

- GCIS flare - the blowdown system from the GCIS unit vents to flare and is burned with a 98% VOC control efficiency;
- area # 3 (off-sites) flare - this is fed by a number of units and has an efficiency of 98%;
- brine pit flare - serves the GCIS storage caverns, which burns vapours released from brine saturated with ethylene or propylene (VOC control efficiency = 98%).

While there were no storage tanks located in the GCIS unit, cavern ethylene storage was included in the storage and loading emissions totals. These caverns are controlled by the brine pit flare described above. Fugitive emissions were calculated using average leak/no leak factors for the GCIS and off-sites sections.

Novacor, Ethylene I and Ethylene II

Novacor operates two ethylene plants at its Joffre site. Both use similar processes to process ethane feedstocks extracted from natural gas to produce ethylene and other byproducts. Process emissions were estimated using both emission factors and source data. The only control equipment specified for process VOC emissions was a flare, which collects vapours from all process vents. The VOC control efficiency of the flare varied from 80% to 99% for each process stream, depending on the composition of the gas. There are no storage tanks or loading operations within the ethylene plants. Instead, all products are sent to a utilities and olefins distribution section for storage and

TABLE III-5 ETHYLENE PLANT EMISSIONS

PLANT		NAME PLATE PRODUCTION CAPACITY	PROCESS	FUGITIVE	STORAGE & LOADING	SPILLS	PLANT TOTAL
Novacor Ethylene I	t/yr	599,000 (Eth)	673.6	157.2	10.2	0.6	841.6
Joffre, Alberta	%		80.0	18.7	1.2	0.1	100.0
Novacor Ethylene II	t/yr	825,000 (Eth)	441.8	137.0	12.4	1.6	592.7
Joffre, Alberta	%		74.5	23.1	2.1	0.3	100.0
Esso Chemical	t/yr	210,000 (Eth)	133.7	673.5	8.7	37.7	853.6
Sarnia, Ontario	%		15.7	78.9	1.0	4.4	100.0
Petromont	t/yr	225,000 (Eth)	664.5	784.0	22.5	8.8	1479.9
Varennes, Quebec	%		44.9	53.0	1.5	0.6	100.0
Total Ethylene	t/yr		1913.6	1751.7	53.8	48.7	3767.8
	%		50.8	46.5	1.4	1.3	100.0

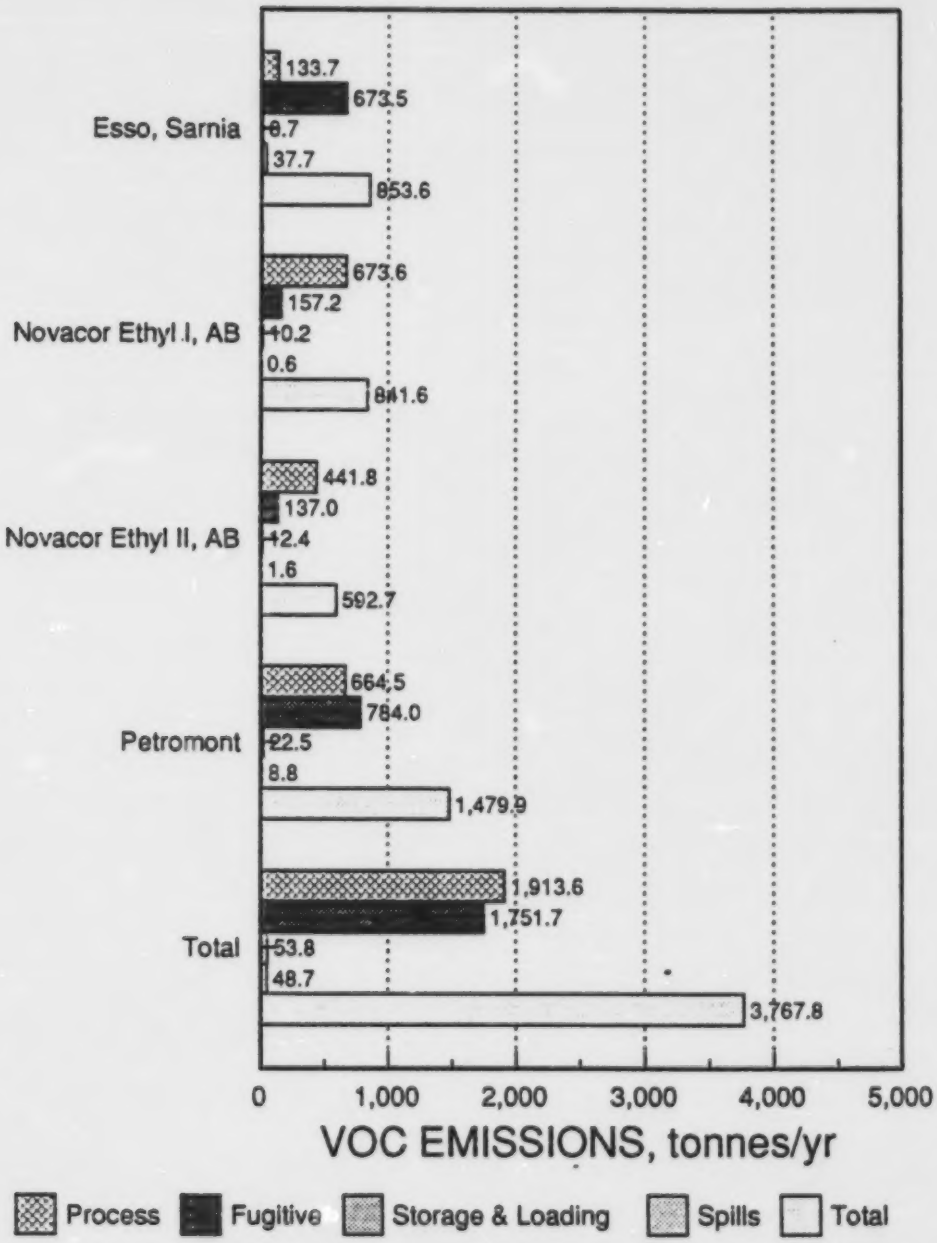


FIGURE III-6 1988 VOC EMISSIONS FROM ETHYLENE PLANTS

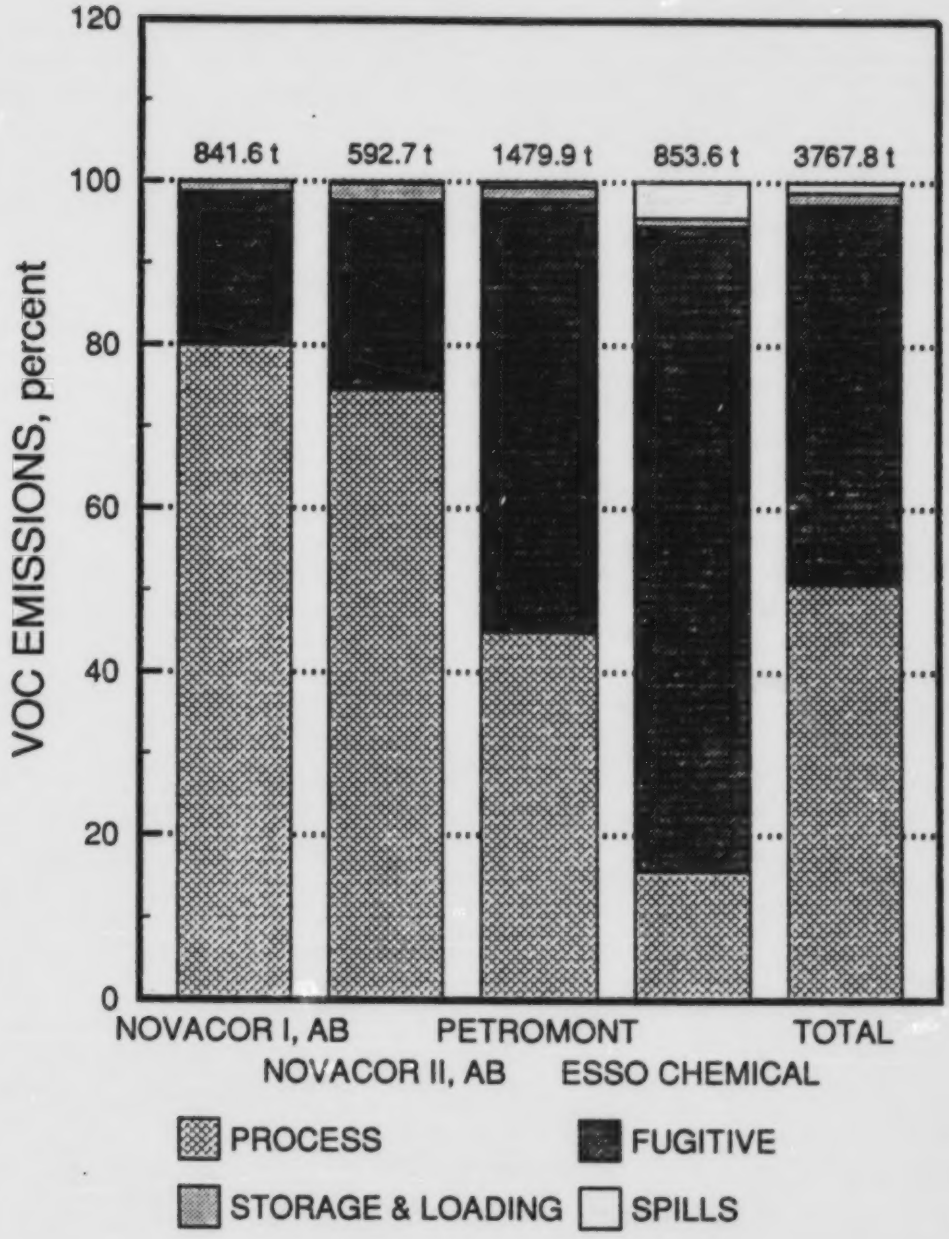


FIGURE III-7 DISTRIBUTION OF VOC EMISSIONS BY SOURCE TYPE FOR ETHYLENE PLANTS

TABLE III-6 ETHYLENE PLANTS - EMISSIONS OF VOCS AND PRIORITY SUBSTANCES

PLANT		VOC	BENZENE	TOLUENE	XYLENE	STYRENE	OTHER
Esso, Sarnia	t	853.6	4.1	0.5	0.2	0.0	848.8[a]
	%		0.5	0.1	0.0	0.0	99.4
Novacor Ethylene I	t	841.6	30.5	2.2	1.0	0.3	807.6[b]
	%		3.6	0.3	0.1	0.0	96.0
Novacor Ethylene II	t	592.7	8.9	0.6	0.1	0.2	582.9[b]
	%		1.5	0.1	0.0	0.0	98.3
Petromont	t	1479.9	45.9	17.6	6.3	3.0	1406.4[c]
	%		3.1	1.2	0.4	0.2	95.0
Total, Ethylene Plants	t	3767.8	89.4	20.9	7.6	3.5	3645.7
	%		2.4	0.6	0.2	0.1	96.8

[a] Emissions are primarily ethylene

[b] Composition of "other" not given for process emissions

[c] Includes ethylbenzene

distribution. The tank emissions were calculated using equations from the U.S. EPA and apportioned to Ethylene I and II in a 45:55 ratio, respectively. Losses from loading were calculated and a 90% control efficiency was applied. All vapours from the U & OD section are sent to the Ethylene I plant flare.

Fugitive emissions for each ethylene plant were calculated using stratified emission factors for valves and flanges. However, all pressure relief valves (PRVs) are sent to flare, so the emission factor for PRVs was reduced by 80%.

The stratified fugitive emissions for Ethylene I and II are 128.3 tonnes and 101.6 tonnes respectively, compared to 356.2 tonnes and 347.3 tonnes calculated using SOCMI factors. Fugitive emissions were calculated using SOCMI factors for the U & OD section, and apportioned to the Ethylene plants in the same 45:55 ratio as for tanks and loading.

Petromont

Petromont's Varennes plant produces ethylene and co-products by thermal cracking of different feedstocks (naphthas, gas oils, butane, propane and a mixed LPG stream was used in 1988). The plant was built in 1963 but most of the equipment now in operation was installed in 1975.

The VOC control equipment in place included:

- flare stack used to burn excess fuel gas (efficiency of 99.5%) and other intermittent hydrocarbon streams (control efficiency of 98%);

- cracked gases lost through the compressor seals are collected using oil traps and a separator pot (control efficiency of 95%).

Process emissions were estimated using emission factors and source data. To estimate emissions coming from the compressor lube oil vent, an emission factor obtained from a report by IT Enviroscience (Lovell et al, 1981) was used. For intermittent process sources, emissions were calculated using specific source data and efficiency of the flare (where applicable).

Emissions from tanks and loading were calculated using U.S. EPA equations. From those calculations, more than 60% of the storage and loading emissions originate from gasoline loading. The loading of lighter fractions involves the use of a vapour recovery system, with an efficiency of 98% to 99%.

Fugitive emissions were calculated by plant section using SOCMI factors. Component counts were done both on-site and from process and instrumentation diagrams.

4. Ethylene Oxide/Ethylene Glycol Plants

VOC emissions from the three selected ethylene oxide/ethylene glycol plants are shown in Table III-7 and graphed in Figures III-8 and III-9.

Table III-8 shows the breakdown of VOC emissions into priority substance list chemicals. There are no emissions of benzene, toluene, xylenes or styrene at the EO/EG plants surveyed.

Dow, Fort Saskatchewan

Dow's Fort Saskatchewan plant produces ethylene oxide and ethylene glycol from ethylene, oxygen and ballast gas. Dow has completed an in-house study of emissions, and data for the CCPA study was extracted from this. As a result, much of the data for the Dow plant is not reported in the format of the data sheets used for this study, and base data is, for the most part, not available.

Emissions from continuous and intermittent process vents were measured. No specific emission controls are in place; the original process design minimized emissions through recirculation of various process streams. Emissions from storage tanks and loading operations were reported to be zero, due to recovery methods practised. Any losses from the storage area are from fugitive sources. These are calculated for the entire plant using equipment counts and SOCMI factors. Also reported were emissions included as "other", which were predominantly due to equipment openings, sampling devices and PRVs. As such, these were included as intermittent process emissions.

Union Carbide, Prentiss, Alberta

Union Carbide's Prentiss plant produces ethylene oxide and ethylene glycol from ethylene, oxygen and other feeds. Process emissions were estimated based on source testing and design data. All "significant VOC containing vent streams", (both high and low calorie waste gases) are collected and incinerated in the plant's boilers with a 99% VOC control efficiency. However, base data was not supplied and the process streams to which this control applies is not known. No other VOC control equipment is in place, since the plant was built with at-source reduction where possible.

Fugitive emissions were estimated based on equipment counts from line isometrics and flow sheets, and SOCMI factors. All storage was in fixed roof tanks, but the emission calculation method used is unknown. Similarly, for loading operations, only total emissions were given with no base data.

Union Carbide, Montreal-East

The Union Carbide plant in Montreal produces ethylene oxide and ethylene glycol. There are three distinct process units on site: ethylene oxide; ethylene glycol Unit 1 and ethylene glycol Unit 2. However, while process emissions are broken down by process

TABLE III-7 ETHYLENE OXIDE/ETHYLENE GLYCOL PLANT EMISSIONS

PLANT		NAME PLATE PRODUCTION CAPACITY	PROCESS	FUGITIVE	STORAGE & LOADING	SPILLS	PLANT TOTAL
Dow Chemical	t/yr	not given	80.9	91.4	0.0	0.0	172.3
Fort Saskatchewan	%		46.9	53.1	0.0	0.0	100.0
Union Carbide	t/yr	229,460 (EG)	599.6	66.5	0.5	0.4	666.9
Prentiss, Alberta	%		89.9	10.0	0.1	0.1	100.0
Union Carbide	t/yr	70,000	133.0	3.0	0.6	0.2	136.8
Montreal, Quebec	%		97.3	2.2	0.5	0.1	100.0
Total	t/yr		813.5	160.9	1.1	0.5	976.0
	%		83.4	16.5	0.1	0.1	100.0

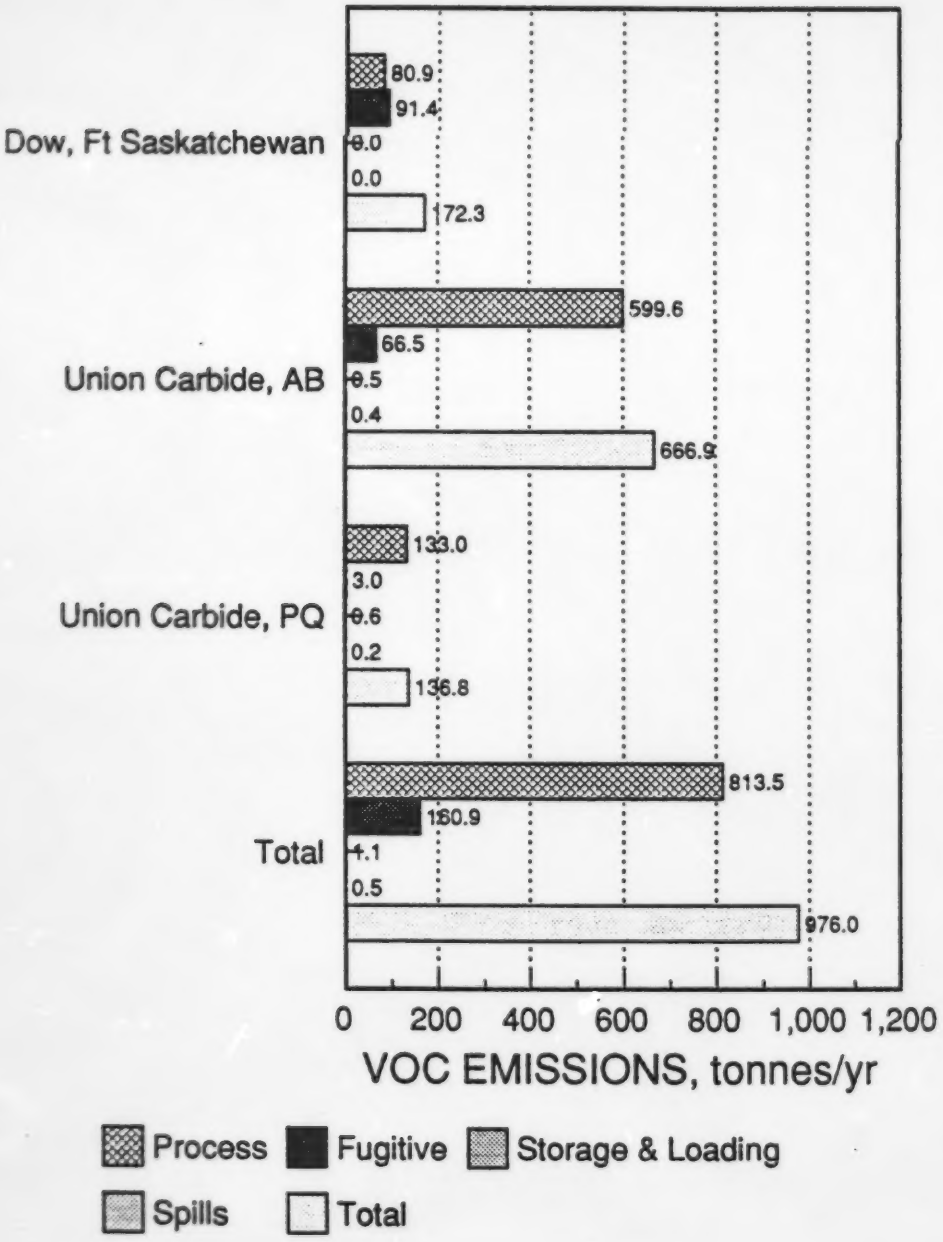


FIGURE III-8 1988 VOC EMISSIONS FROM ETHYLENE OXIDE/ETHYLENE GLYCOL PLANTS

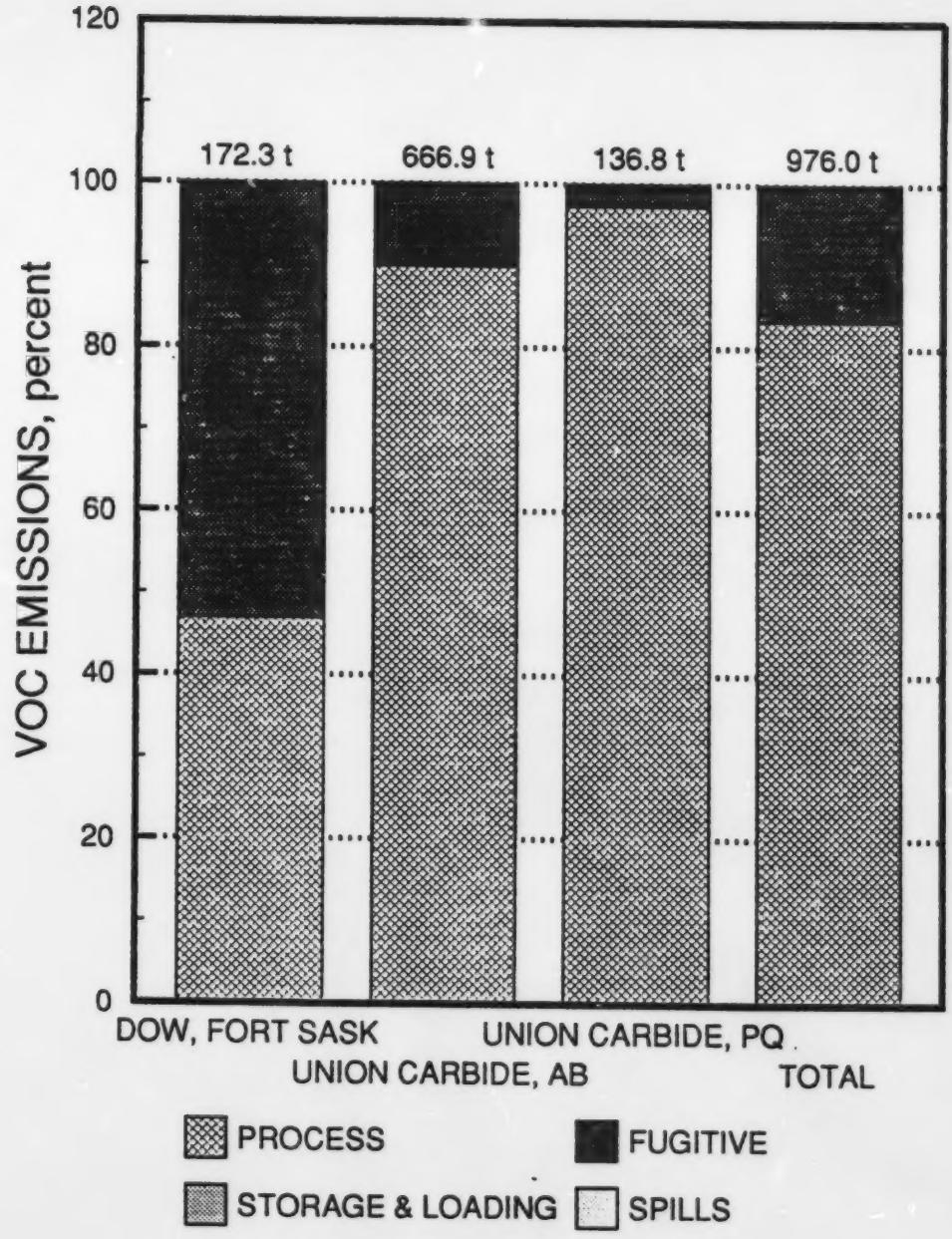


FIGURE III-9 DISTRIBUTION OF VOC EMISSIONS BY SOURCE TYPE FOR ETHYLENE OXIDE/ETHYLENE GLYCOL PLANTS

TABLE III-8 ETHYLENE OXIDE/ETHYLENE GLYCOL PLANTS - EMISSIONS OF VOCs AND PRIORITY SUBSTANCES

PLANT	VOC (t)	COMPOSITION (NO PSL CHEMICALS REPORTED)
Dow, Fort Saskatchewan	172.3	Ethylene, ethylene oxide, ethylene chloride and non-PSL chemicals
Union Carbide, Red Deer, Alberta	666.9	Ethylene oxide, ethylene glycol and non-PSL chemicals
Union Carbide, Montreal, Quebec	136.8	Ethylene oxide, ethylene, vinyl chloride, ethylene dichloride and non-PSL chemicals
Total, EO/EG Plants	976.0	

unit, storage tank, loading and fugitive emissions are not. Consequently, emissions are reported as a total of the three units.

Process emissions originate from various process vents and are estimated by source measurements. No VOC control equipment was specified. Fugitive emissions were calculated in two ways: first, using SOCMI factors and second, using Union Carbide's own emission factors, which were derived from an in-house study. The fugitive emissions reported here, 2.97 tonnes/yr, were derived from the latter method. The SOCMI method would yield 131.9 tonnes/yr. The plant has only fixed roof tanks which are vented to a gas scrubber. Loading rack emissions are also vented to this scrubber, which has a VOC recovery efficiency of 99%.

5. Polyethylene Plants

VOC emissions from the seven selected polyethylene plants are shown in Table III-9 and Figure III-10. The individual plants produce different grades of polyethylene, including high density, low density and linear low density. Figure III-11 illustrates the variability of the emissions from the surveyed source types, which results to some degree because of differences in the processes used.

Emissions of priority substance list chemicals are given in Table III-10. There are no benzene, toluene, xylene or styrene emissions reported from the surveyed plants.

Dow, Fort Saskatchewan

Dow produces linear low density polyethylene by the solution polymerization process at Fort Saskatchewan. Process emissions originate from product handling, and were calculated from source measurements, mass balance and estimates. Any ethylene purged from the process is sent to either:

- furnace - fired by fuel gas and an ethylene purge stream (VOC destruction efficiency not given);
- flare - burns purged ethylene, hydrocarbons collected from process emergency relief devices, and losses from purification beds.

The remainder of the emissions were reported as totals, without base data. Fugitive emissions were calculated using SOCMI factors, while the methodology for storage and handling was not given.

Dupont

Dupont produces both high density and linear low density polyethylene resins in each of two plants at its Corunna site using a solution polymerization process. The original plant was constructed in 1959 and the second in 1975.

TABLE III-9 POLYETHYLENE PLANT EMISSIONS

PLANT		NAME PLATE PRODUCTION CAPACITY	PROCESS	FUGITIVE	STORAGE & LOADING	SPILLS	PLANT TOTAL
Dow Chemical	t/yr	not given	59.0	79.6	1.2	0.0	139.7
Fort Saskatchewan	%		42.2	56.9	0.8	0.0	100.0
Dupont	t/yr	235,000	1687.0	988.0	25.8	0.0	2700.8
Corunna, Ontario	%		62.5	36.6	1.0	0.0	100.0
Esso Chemical	t/yr	180,000	86.3	23.2	0.0	0.1	109.6
Sarnia, Ontario	%		78.7	21.2	0.0	0.1	100.0
Novacor	t/yr	386,000 (LLDPE)	87.3	420.3	2.9	0.0	510.5
Joffre, Alberta	%		17.1	82.3	0.6	0.0	100.0
Dow Chemical LDPE	t/yr	not given	41.0	52.0	90.0	0.0	183.0
Sarnia, Ontario	%		22.4	28.4	49.2	0.0	100.0
Dow Chemical HDPE	t/yr	not given	199.0	48.0	0.0	0.0	247.0
Sarnia, Ontario	%		80.6	19.4	0.0	0.0	100.0
Novacor	t/yr	105,000 (HDPE)	136.8	150.3	0.2	0.4	287.6
Moore Township, Ontario	%	90,000 (LDPE)	47.6	52.2	0.1	0.1	100.0
Total	t/yr		2296.4	1761.3	120.0	0.5	4178.3
	%		55.0	42.2	2.9	0.0	100.0

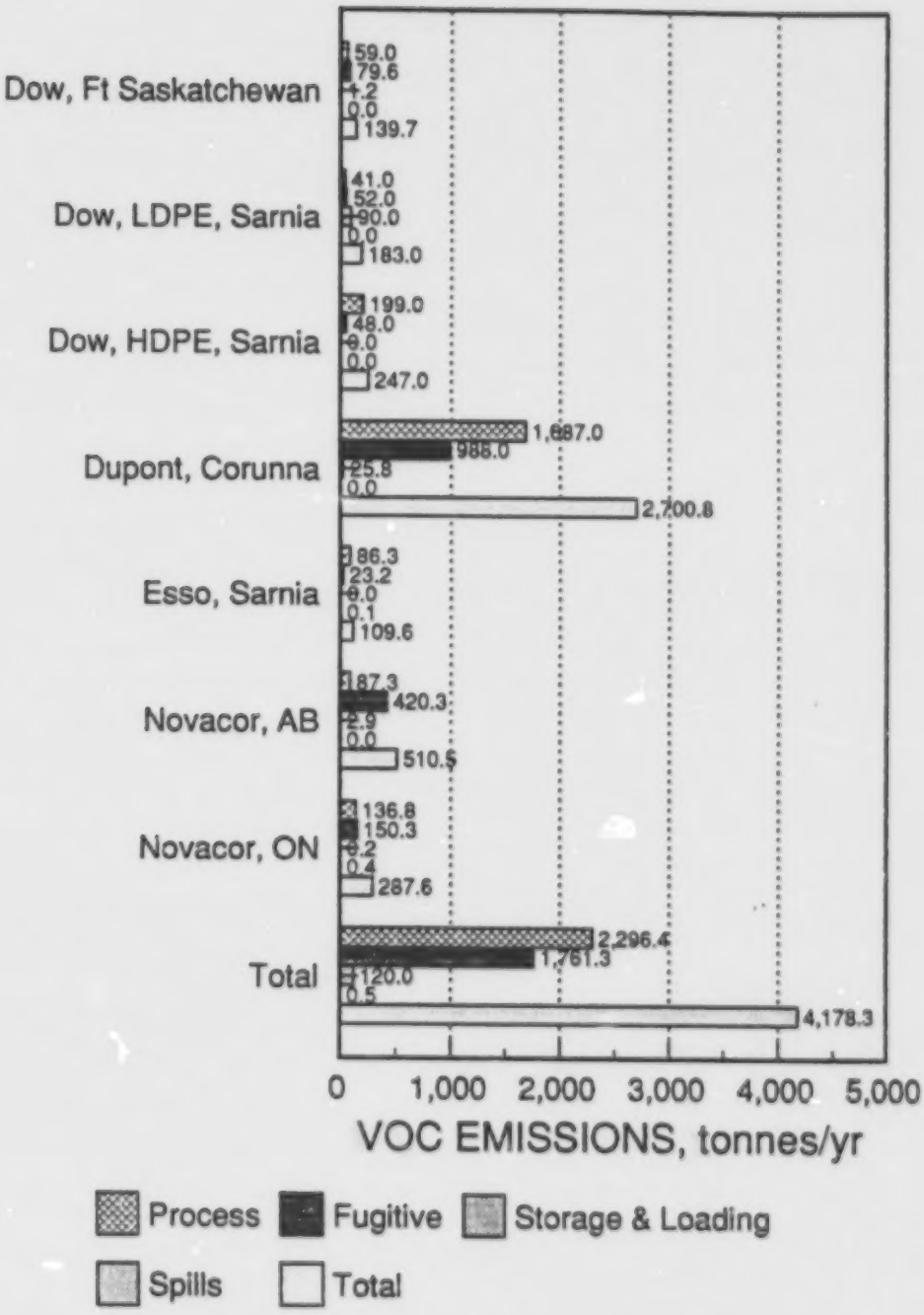


FIGURE III-10 1988 VOC EMISSIONS FROM POLYETHYLENE PLANTS

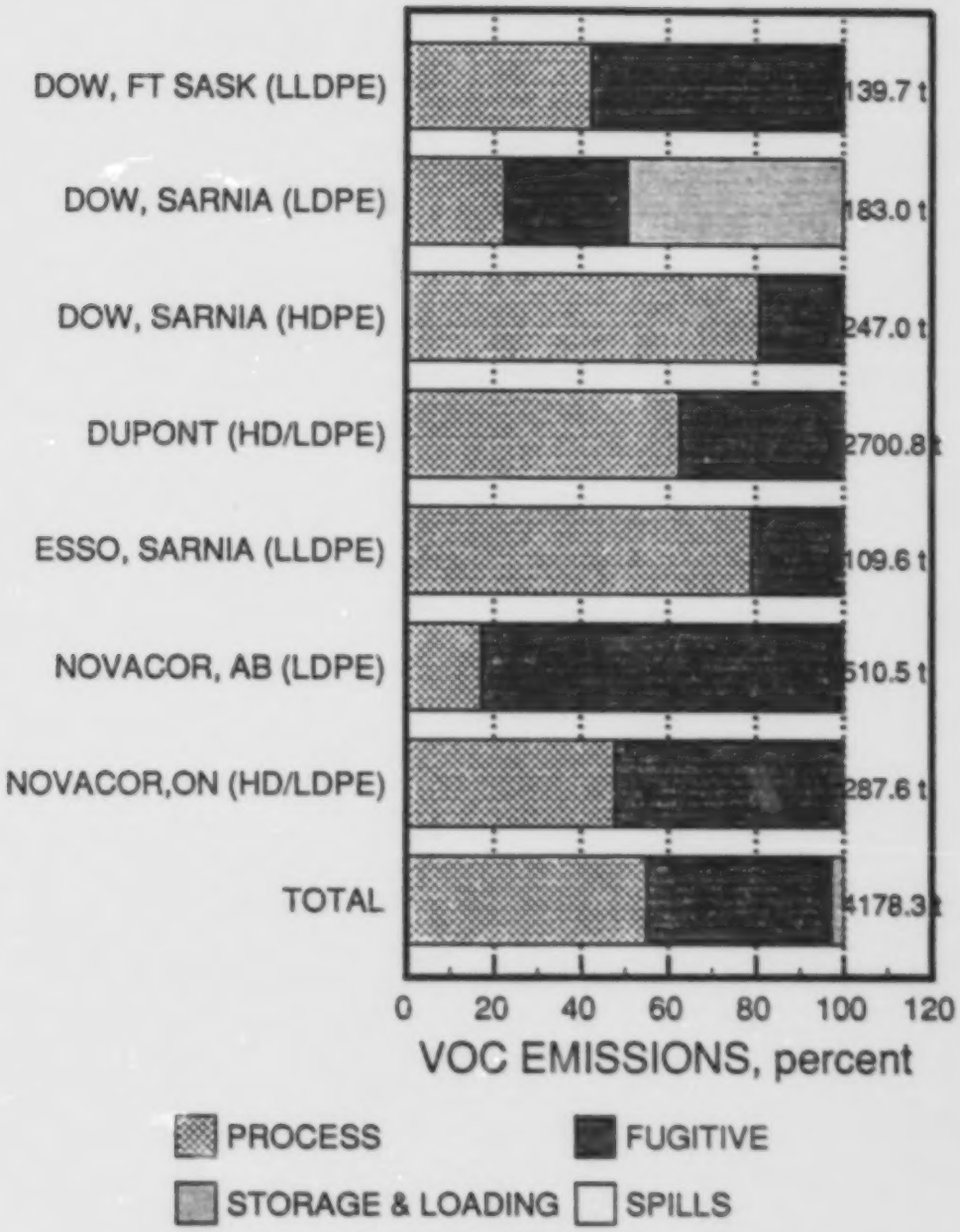


FIGURE III-11 DISTRIBUTION OF VOC EMISSIONS BY SOURCE TYPE FOR POLYETHYLENE PLANTS

TABLE III-10 POLYETHYLENE - EMISSIONS OF VOCs AND PRIORITY SUBSTANCES

PLANT	VOC (t)	VOC COMPOSITION (NO PSL CHEMICALS REPORTED)
Dow, Fort Saskatchewan	139.7	Ethylene and a non-PSL hydrocarbon carrier
Dow, Sarnia HDPE	183.0	Ethylene and other non-PSL organics (details not given)
Dow, Sarnia LDPE	247.0	Ethylene and other non-PSL organics (details not given)
Dupont	2700.8	
Esso, Sarnia	109.6	Primarily ethylene, with ethane, butane, butene, isopentane, hexene
Novacor, Joffre	510.5	Ethylene, butene, isopentane and non-PSL chemicals
Novacor, Moore Township	287.6	Primarily ethylene, with small amounts of isopropyl alcohol, propylene, ethane
Total, Polyethylene Plants	4178.3	

Process emissions were both measured and estimated, with the majority being measured. More than 90% of the process emissions are from the older plant. Although both plants utilize the same polymerization technology, they produce a different range of products and the low emission technology used in the newer plant cannot be used in the original plant. A technological route to eliminate the process emissions from the older plant has been identified and is currently in the engineering stage.

All process venting or blowdown, all gas purging for maintenance, and all hydrocarbon relief valves exhaust to a flare stack. The flare is available 100% of the time and, since no specific efficiency data are available, is estimated to have a VOC control efficiency of at least 95%.

Tank car loading and unloading operations are performed in a closed system, with any losses directed to flare. Hence, loading emissions were included under the intermittent process total.

SOCMI factors were used to estimate fugitive emissions.

Esso Chemical Canada, Sarnia Polyethylene Plant

The Esso polyethylene plant produces linear low and high density polyethylene resins using the Unipol™ gas phase process. The plant was started up in 1983 and has a capacity of 180 kt/year. Process emissions include process vents, continuous analyzer vents, and flares. VOC control equipment identified include:

- Process flare - a gas collection and flare system for process and equipment vents. Overall VOC control efficiency is reported to be 99.5%.

- Emergency flare - a gas collection and flare for emergency venting of reaction equipment. Overall VOC control is reported to be 98%.

- Product purging and gas recovery - volatile gases are stripped from the polyethylene. Condensable components are recovered and recycled and the uncondensed materials are vented via the process flare. Minimum VOC control efficiency is reported to be 99.5%.

- Compressor oil degassing - entrained/dissolved ethylene in compressor seal oil is recovered by flash separation and stripping. Overall VOC control efficiency is 98.5%.

Process emissions were calculated based on measured flows and compositions (with the exception of the compressor oil sump vent).

Fugitive emissions totalling 23.2 tonnes annually were based on "stratified emission factors" (using SOCMI factors, the fugitive emissions would be 217.5 t/yr). All hydrocarbon storage is in pressurized drums and any losses/emissions are accounted for

in the flare emissions. There are no volatile hydrocarbon loading operations and off-loading is via totally closed/nitrogen purged systems with all emissions accounted for in the flare.

Novacor, Joffre

Novacor chemicals operates a linear low density polyethylene plant at Joffre, employing Unipol technology. Process emissions were calculated using emission factors and source data. The only identifiable VOC control is a flare system, which gathers all waste hydrocarbon streams via two headers, one for liquids and one for gases. The destruction efficiency was reported as approximately 98%.

Fugitive emissions are calculated using estimated value counts and SOCMI factors. Novacor states that "real fugitive emissions are likely much lower" than that reported. All hydrocarbon containing tanks at the plant, are located in the utilities and olefins distribution section, and these tanks were accounted for in Novacor's adjacent ethylene plants at Joffre. Loading losses are calculated using U.S. EPA equations, and loading rack vapours are recovered and flared.

Novacor, Moore Township

The Novacor Mooretownship Site, in operation since 1976, manufactures both high density polyethylene (Unipol technology) and low density polyethylene (tubular high pressure process).

Process emissions were calculated using specific source data. A flare header system is used to collect and combust most hydrocarbon sources from both polyethylene units. The destruction efficiency of the flare (99.5%) is based upon vendor supplied design specifications.

Fugitive emissions from valves, flanges and pump seals were calculated using SOCMI factors. Pressure relief valve discharges are directed to the flare hence the destruction efficiency was applied to these fugitive emissions.

Tank and loading operation emissions were calculated using U.S. EPA calculation methodologies with no control efficiency applied.

Dow, Sarnia

The Dow plant in Sarnia produces both low density and high density polyethylene, by the solution polymerization process. At the time of this report, details were not available regarding the methods used in calculating emissions. Only emission totals were reported, with all data having been extracted from an in-house emissions study. Process emissions were calculated using measured data, engineering estimates and process modelling. Fugitive emissions were estimated using primarily Method I for LDPE, although Method II was used for certain equipment. For the HDPE process, Method I

was also used, with Method III used for ethylene emissions. No information was available with respect to tanks and loading operations.

6. Maleic Anhydride Plants

Only one maleic anhydride plant is in operation in Canada. Its emission totals are shown in Table III-11 and Figure III-12. Speciation of the VOC emissions is shown in Table III-12.

Monsanto

Monsanto's maleic anhydride unit operates primarily in batch mode. For reasons of confidentiality, no base data was supplied. The emissions reported here are given as totals only. Process emissions were estimated from source measurements and material balance calculations. A scrubber is used in the product recovery step, but the VOC control efficiency was not given. The unit has only one fixed roof tank, and no loading operations. Fugitive emissions were determined using equipment counts and SOCMI factors.

7. Ethylbenzene/Styrene Plants

VOC emissions from styrene/ethylbenzene plants are tabulated in Table III-13 and graphed in Figure III-13. The variation in the proportion of process, fugitive, storage and loading and spill emissions between plants is shown in Figure III-14.

Speciation of the VOC emission into priority substance list chemicals are shown in Table III-14.

Dow, Sarnia

Dow's Sarnia plant produces ethylbenzene and styrene. At the time of this report, only emission totals were available. Partial information was available on the methods used for estimating VOC emissions, which were extracted by Dow staff from an in-house emissions study. Process emissions were calculated using measured data, engineering estimates and process modelling. Fugitive emission estimates were obtained using Method III, except for ethylene emissions, which were determined using Method II. Information was not available on the methods used for estimating tankage and loading emissions.

Polysar

The Polysar plant at Sarnia produces ethylbenzene and styrene at its two distinct process units on-site. Ethylbenzene, obtained from ethylene and benzene, is dehydrogenated to crude styrene which is then purified to yield styrene monomer.

TABLE III-11 MALEIC ANHYDRIDE PLANT EMISSIONS

PLANT		NAME PLATE PRODUCTION CAPACITY	PROCESS	FUGITIVE	STORAGE & LOADING	SPILLS	PLANT TOTAL
Monsanto	t/yr	not given	77.1	7.5	4.6	0.0	89.2
LaSalle, PQ	%		86.4	8.4	5.1	0.0	100.0

TABLE III-12 MALEIC ANHYDRIDE PLANTS - EMISSIONS OF VOCs AND PRIORITY SUBSTANCES

PLANT		VOC	BENZENE	XYLENE
Monsanto	t	89.2	63.4	25.9
	%		71.0	29.0

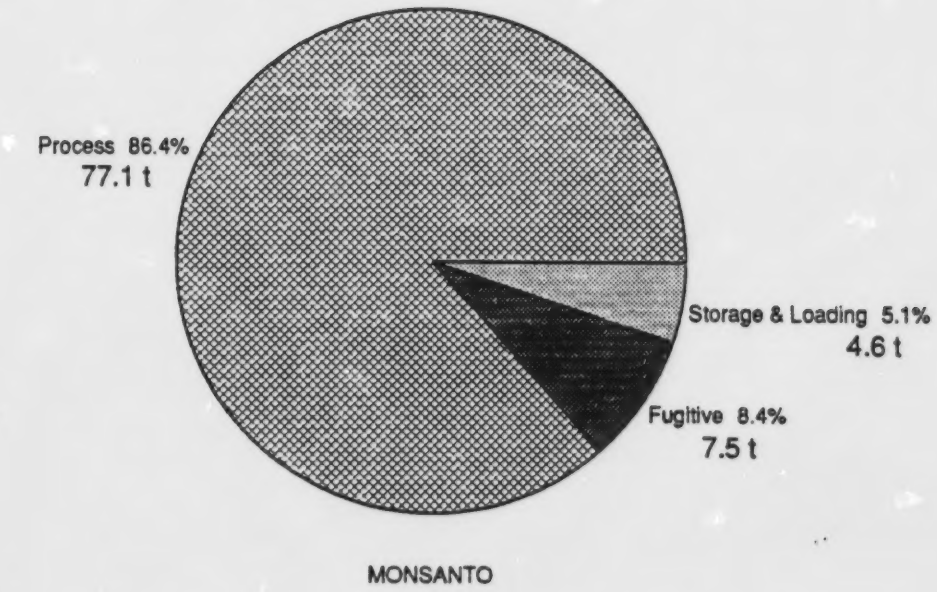


FIGURE III-12 1988 VOC EMISSIONS FROM MALEIC ANHYDRIDE PLANTS (1)

TABLE III-13 ETHYLBENZENE/STYRENE PLANT EMISSIONS

PLANT		NAME PLATE PRODUCTION CAPACITY	PROCESS	FUGITIVE	STORAGE & LOADING	SPILLS	PLANT TOTAL
Dow Chemical	t/yr	not given	105.0	2.0	88.0	0.0	195.0
Samia, Ontario	%		53.8	1.0	45.1	0.0	100.0
Polysar	t/yr	303,000 (EB)	176.1	59.0	91.0	0.3	326.3
Samia, Ontario	%	272,000 (Sty)	54.0	18.1	27.9	0.1	100.0
Shell, Scotford	t/yr	380,000 (Sty)	1.4	193.6	16.7	5.6	217.2
Fort Saskatchewan	%		0.6	89.1	7.7	2.6	100.0
Total	t/yr		282.4	254.6	195.7	5.8	738.5
	%		38.2	34.5	26.5	0.8	100.0

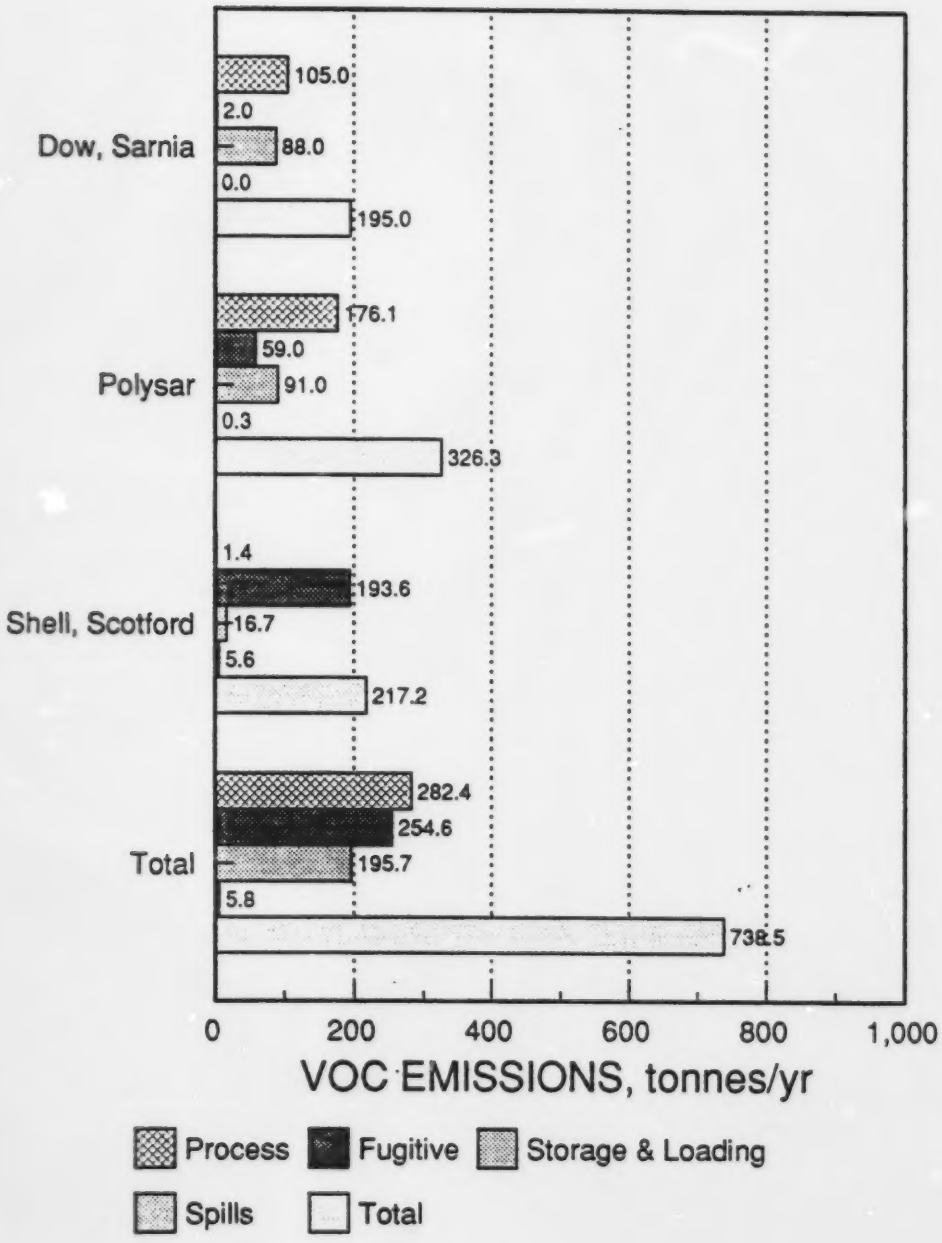


FIGURE III-13 1988 VOC EMISSIONS FROM ETHYLBENZENE/STYRENE PLANTS

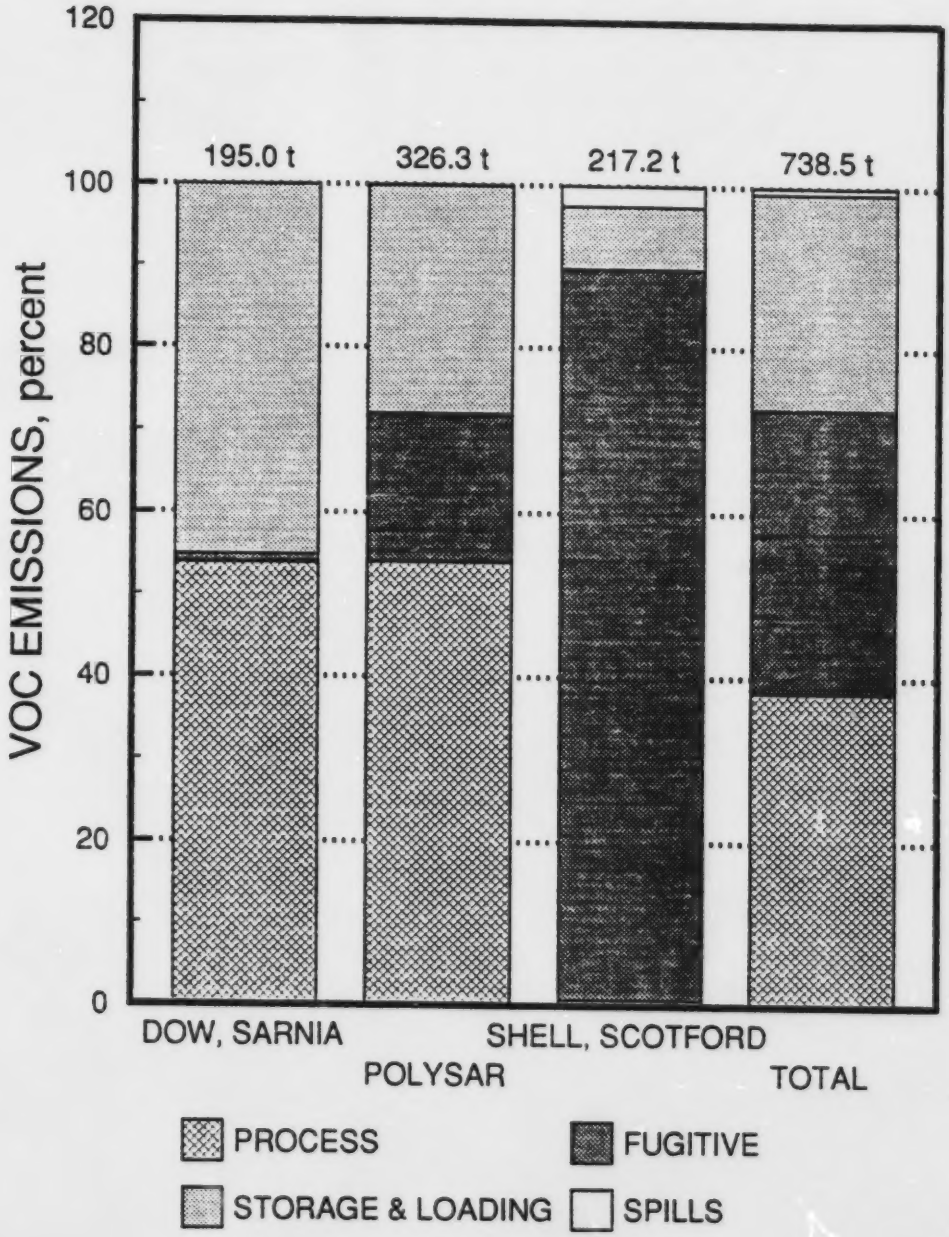


FIGURE III-14 DISTRIBUTION OF VOC EMISSIONS BY SOURCE TYPE FOR ETHYLBENZENE/STYRENE PLANTS

TABLE III-14 STYRENE/ETHYLBENZENE PLANTS - EMISSIONS OF VOCS AND PRIORITY SUBSTANCES

PLANT		VOC	BENZENE	TOLUENE	STYRENE	OTHER
Dow, Sarnia	t	195.0	77.0	7.0	26.0	85.0
	%		39.5	3.6	13.3	43.6
Polysar	t	326.3	108.4	9.6	21.8	186.5
	%		33.2	2.9	6.7	57.2
Shell, Scotford	t	217.2	0.7	0.0	16.4	200.1
	%		0.3		7.6	92.1
Total, EB/ Styrene Plants	t	738.5	186.1	16.6	64.2	471.6
	%		25.2	2.2	8.7	63.9

Process emissions originate from process vents, hotwells and stacks on flare and two process heaters. Discharges from all process vents and from relief valves are collected in a dedicated flare system. The flare destruction efficiency was reported to be 99%.

Emissions from hotwells on vacuum equipment, after partial condensation, vent to atmosphere. Process emissions were determined using source testing data, process data, and best engineering estimates.

Emissions from tanks and loading operations were calculated using U.S. EPA equations, with no recovery efficiencies applied.

Fugitive emissions estimates were obtained for the plant in eight blocks and totalled, using stratified emissions factors and on-site count and testing of components. By such estimate, the total fugitive losses amount to 59 tonnes/year whereas, when using SOCMI factors, the fugitive losses would amount to 215 tonnes/year.

Shell, Scotford

Shell produces ethylbenzene and styrene at its Scotford complex from ethylene and benzene. Process emissions were determined using source testing data. The VOC control equipment in place includes:

- styrene process flare - all relief valves are routed to the flare for combustion (control efficiency = 85% to 90%);
- activated carbon filter - removes vented hydrocarbons stripped from contaminated water (control efficiency = 99%);
- all waste streams from the ethylbenzene or styrene units are either recycled or used as boiler fuel.

Emissions from tanks were calculated using U.S. EPA methodologies. Emissions of benzene vapours are controlled by a benzene vapour recovery system, which condenses recovered vapours and returns them to storage. Loading emissions were calculated using U.S. EPA equations with no recovery efficiency applied.

Fugitive emissions were calculated using leak/no leak factors. These fugitive losses were considered to be uncontrolled, and the actual total reported is lower due to the use of various fugitive control technologies at Scotford. For example, fugitive emissions from pressure relief valves and sampling connections were reduced by 85% to account for venting to flare. 100% emission control efficiency was used for double pump seals. Fugitive losses were also calculated using SOCMI factors, with the same control efficiency factors applied. SOCMI factors gave fugitive emissions of 705.5 t/yr, compared to 193.6 t/yr using leak/no leak methods.

C. Comparison of Fugitive Emission Estimation Methods

A number of the plants participating in the study used factors other than SOCMI to estimate fugitive emissions. The results obtained using the different methods are shown in Table III-15 and graphed in Figures III-15. In a number of cases, emission factors for specific equipment elements were multiplied by a factor to account for a control device. In these cases, the same control efficiency factor was applied to the result calculated using SOCMI emission factors. The pronounced decrease in the estimate of fugitive emissions resulting from use of a more rigorous methodology suggests SOCMI emission factors yield an over-estimate.

D. VOC Emission Controls in Use

This section presents a brief overview of VOC emission control equipment and methods for process, fugitive, and storage and handling sources. A discussion of VOC control options available for chemical plants is given in Chapter IV.

1. Process Sources

Each of the surveyed plants practice some form of VOC emission control, whether it be inherent to the process or through the use of specific control equipment.

The most common VOC control equipment in place are flares, and the reported VOC destruction efficiency reported for these ranged from 80% to greater than 99%. Table III-16 summarizes the flares reported in use for the survey. An average control efficiency, calculated from 14 flares reported, was 96.2%. Efficiency values were based largely on engineering estimates, although some were from literature or manufacturer's specifications. The literature (Pohl and Soelberg, 1985) suggests that flare flame combustion efficiencies can be very high, exceeding 98%, but varies from 55% to 100% in practice. The efficiency is dependent on a number of factors, specifically:

- operating conditions
- steam or air injection
- flame stability
- flare size and flare design

A number of plants included boilers, heaters, incinerators and furnaces as VOC control equipment. By definition, any combustion source using a VOC stream primarily for its fuel value was not included as a VOC control. However, those that incinerated or combusted waste VOC streams that would otherwise have vented to atmosphere, were included as VOC control equipment. In general, the destruction efficiencies reported for fired heaters and furnaces were high, typically 97% to 100%.

Other methods of controlling process VOC emissions included scrubbers and activated carbon filters. Some of the newer plants have incorporated VOC emission

TABLE III-15 COMPARISON OF FUGITIVE EMISSION ESTIMATION METHODS

PLANT	FUGITIVE ANNUAL VOC EMISSIONS (t/yr)			
	SOCMI FACTORS	OTHER METHODS	PERCENT REDUCTION (%)	OTHER METHOD USED
Esso, Sarnia Polyethylene	217.5	23.2	89.3	Stratified
Shell, Scotford Styrene	705.5	193.6	72.6	Leak/No Leak
Union Carbide, Montreal, EO/EG	131.9	3.0	97.7	Union Carbide[a] Corporation emission factors
Novacor, Joffre				
Ethylene I	356.2	128.3	64.0	Stratified[b]
Ethylene II	347.3	101.6	70.7	
Polysar, Sarnia EB/Styrene	215.0	59.0	72.6	Stratified
Dow, Sarnia EB/Styrene	108.3	22.8	78.9	Leak/No Leak
		2.1	98.1	Stratified

[a] Emission factors from Union Carbide Corporation studies

[b] Stratified data for valves and flanges only

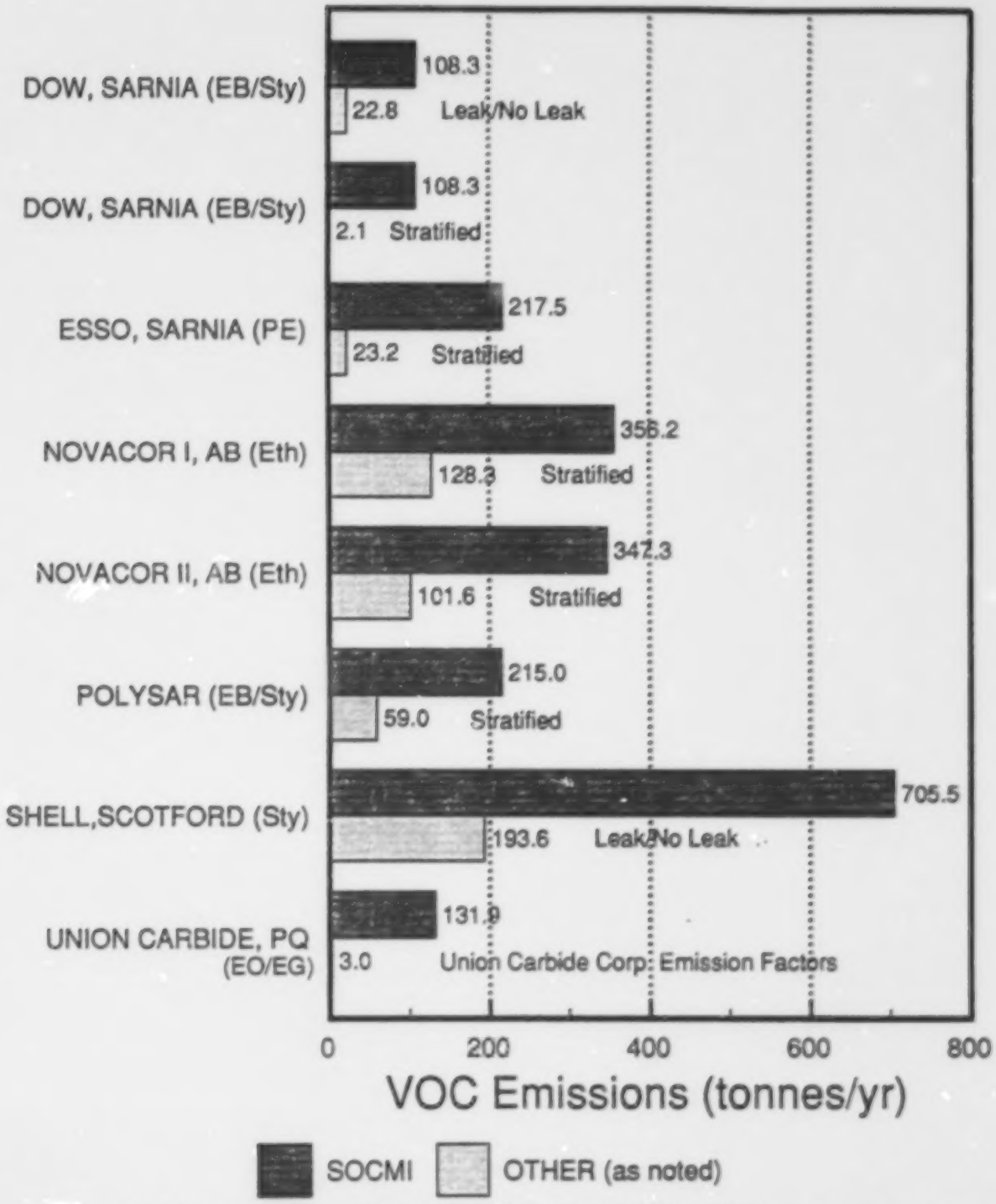


FIGURE III-15 COMPARISON OF FUGITIVE EMISSION ESTIMATES MADE USING ALTERNATE METHODS

TABLE III-16 SUMMARY OF FLARES IN USE

PLANT	FLARE	REPORTED VOC CONTROL EFFICIENCY (%)	SOURCE OF EFFICIENCY ESTIMATE
Dow Chemical Fort Saskatchewan, Alberta	Flare	not given	not given
Dow Chemical Sarnia, Ontario	Flare-HDPE Flare-LDPE	98.3 - 98.5 not given	not given not given
Dupont Corunna, Ontario	Flare (steam assisted, natural gas pilot)	95	engineering
Esso Chemical Sarnia, Ontario	Brine Pit Flare # 2 GCIS Flare Area # 3 Process Flare Emergency Flare SPEP Flare	98 98 98 98 99.6	engineering engineering engineering engineering engineering
Novacor Joffre, Alberta	Ethylene I Flare (steam assisted, natural gas pilots) Ethylene II Flare (steam assisted, natural gas pilots) Polyethylene Flare (air assisted)	80 - 99 80 - 99 98	engineering engineering engineering
Novacor Moore Township, Ontario	Flare System (steam assisted)	99.5	supplier
Petromont Varennes, PQ	Flare (steam assisted)	99.0	literature
Polysar Sarnia, Ontario	Flare (steam assisted)	99.0	supplier
Shell Scotford, Alberta	Styrene Process Flare	85 - 90	engineering

controls into their process designs, through recycling of overhead vapours back into the process.

2. Fugitive Sources

Descriptions of inspection and maintenance procedures and general fugitive emission control practices were requested from all plants. An overview of the practices employed are best described by each type of equipment, as follows:

Valves

- regularly scheduled leak inspection and maintenance
- use of ball valves or those which are equally effective
- upgraded packing

Pump Seals

- regularly scheduled leak inspection and maintenance
- use of double seals on pumps in priority substance service (eg., benzene)
- double mechanical seals complete with leak detector sensors on rotating equipment

Compressor Seals

- regular inspection (eg., twice daily) for signs of problems, and preventative maintenance
- recovery of compressor seal leakage for reprocessing or flaring
- log sheets filled out for large compressors, to aid in anticipating potential problems

Pressure Relief Seals

- pressure relief valves discharge to flare
- leakage from pressure relief seals gathered and sent to flare
- leak inspection on a regular basis

Flanges

- regular inspection programs
- flanges torqued down hot after start-up
- flanges and packings "sniffed" and repaired as necessary
- finish specifications for flange faces
- flanges leaking while "on-line" are clamped and leak sealing compounds are used

Open-Ended Lines

- plugged or blanked when not in use
- regularly scheduled inspection

Sampling Connections

- closed loop sampling
- return connections on sampling points to process or flare

General Practices

- regularly scheduled inspection and maintenance
- routine preventative maintenance
- annual turnaround
- gas detectors mounted in critical areas to detect leaks, detectors tied in to control room
- in-plant benzene monitoring systems
- welded or flanged fittings used on pipes in hydrocarbon service, as opposed to threaded connections
- seal welding of threaded connections where leaks cannot be tolerated
- closed flushing system used on mechanical equipment prior to maintenance
- comprehensive metallurgical inspection programs
- computerized safety inspection and testing systems
- one button emergency shut-down systems
- process interlocks and isolation systems

3. **Storage and Loading Sources**

A number of control methods have been reported for emissions from tanks. These include:

- tank insulation or refrigeration
- lowering of stock vapour pressure
- use of floating roof tanks
- benzene vapour recovery systems
- scrubbing of tank vent vapours
- incineration of tank vent vapours
- vent condensers

Control methods for loading operations include:

- vapour recovery units
- scrubbing of loading losses
- incineration of loading losses

- performing loading in a closed, pressurized system with losses sent to flare
- flaring of hydrocarbon liquids left over in loading hoses

E. Gaps in Available Data and Methods

1. Process Sources

Estimates of emissions from process sources were usually done using specific process data obtained sometimes by measurement, but most often from process and design data. The accuracy of the inventory of VOCs and particulary PSL chemicals could be improved by greater use of measured flow rates and concentrations for process sources.

In a number of cases, respondents included in their response emissions from stationary combustion sources burning plant fuel gas and emissions of methane present in discharge streams. Future inventories should ensure that these emissions are excluded. However, emissions of VOCs resulting from destruction of waste gas streams in boilers or fired heaters should be included if this is the means of VOC emission control.

Most emissions from process sources listed by respondents were determined using specific data for the discharge stream. These can seldom be associated with an EPA source classification code, precluding comparison of calculated emissions with those estimated by an emission factor technique. Such a comparison is made more difficult by the general lack of production related data in the initial plant responses, which is essential for use of EPA emission factors. Although emissions calculated from source specific data can be expected to be more reliable than those calculated using emission factors, the latter does provide a useful check and, if found to be reliable, would require less effort in future if used to prepare updated estimates of emissions. Further work would be needed to rationalize the process emissions calculated for each plant and the corresponding source classification code and emission factor. In addition, the industry would have to provide the base quantities appropriate for each emission factor.

More measured data is needed on the speciation of process emissions. Much of the data provided in the survey is based on design data and engineering estimates.

Wide use is made of flares for destruction of organics before release to the atmosphere. The VOC emissions calculated for flares are very sensitive to the destruction efficiency used, which averaged about 98% in the survey responses. An estimate of emissions can double by simply decreasing the destruction efficiency from 99% to 98%, illustrating the importance of having a reliable average value. None of the respondents had access to a measured values for flare destruction efficiency. All values were obtained either from the flare supplier, or by some type of engineering

estimate. Field measurements are needed to verify that actual flare destruction efficiencies for waste gases at organic chemical plants are in the range of those indicated by suppliers and other sources. This is a difficult undertaking because of the variability of actual operating conditions and technical problems associated with measurement of destruction efficiency, as evidenced by the studies of flares undertaken by the U.S. EPA.

2. Fugitive Sources

Fugitive emissions were calculated for all plants using at least the SOCMI emission factors and in several cases, more sophisticated and resource intensive methods. The main gaps in the data for fugitive emissions are:

- Most plants did not report fugitive emissions by major plant sections, though all reported results for the plant as a whole.

- There was considerable variability in the means used to count equipment including partial counts from drawings augmented by factored estimates of smaller components, counts from drawings supplemented and verified by field surveys, and full field counts of components. This variability makes comparison of results between plants subject to the methodology used. Acceptance of a standard technique for counting equipment would improve the reliability of emission estimates.

- Some plants used SOCMI only, while others used more sophisticated methods. Because of the large differences between fugitive emission estimates made using the different methods, future surveys should be done using one method which yields acceptable estimates.

- Estimates of the composition of fugitive VOC emissions needs to be improved. This would likely require reporting the emissions by major process section so that representative average VOC compositions can be calculated on the same basis.

3. Storage and Loading Sources

Emissions from storage tanks were determined using correlations originally developed for gasoline and crude oils having much higher vapour pressures than many stocks stored at the plants surveyed. Improved correlations for organic chemicals having vapour pressures below 10 kPa would improve the accuracy of the inventory of emissions from storage tanks, but likely not affect the total VOC inventory from the surveyed plants significantly because of their relatively small contribution to the total.

Additional measured data on the composition of VOC emissions would be beneficial and would improve the estimates of emissions of PSL chemicals from storage sources.

The most significant gap in the data for loading emissions is the lack of reliable correlations for loading losses from barges and ships. This gap needs to be rectified for future inventories. Testing to verify or improve the VOC emission correlations used for tank trucks and rail tank cars in a Canadian climate would be very beneficial to future inventories, and improve confidence in the inventory results for the organic chemical industry and be useful, as well, for inventories of the petroleum refining sector.

IV. TECHNOLOGIES/OPTIONS AVAILABLE FOR THE CONTROL OF VOC EMISSIONS

Control of VOC emissions from the organic chemical manufacturing industry is not new. Most companies contacted in the survey make extensive use of control devices and internal recovery and recirculating within processes. Numerous studies have generated a wealth of information dealing with VOC controls and related issues. Consequently, for the purposes of this study there would be little benefit in conducting an exhaustive evaluation of all aspects of VOC control technology. Instead, the intent of this chapter is to give a brief overview of the technologies available, together with up-to-date information on the controls in use and the controls that the CCPA industries are considering. This section describes the controls in-use, their VOC reduction efficiency and, where data was available, costs of control. The level of detail reported on these controls is consistent with the information provided in the survey data sheets and what could be obtained by telephone. It should be noted that VOC emissions can be (and frequently are) reduced internally through process control optimization, reformulation, feedstock changes, etc. but this report will not focus on details of these pollution abatement techniques.

The discussion of VOC controls is organized by source type: process emissions; storage emissions; stock loading emissions; and fugitive emissions. The control options emphasized in this chapter are:

- combustion
- adsorption
- absorption
- condensation
- process modifications
- equipment modifications.

A. Control of Process Vent Emissions

1. Combustion

Combustion devices are the most common form of VOC control in the chemical manufacturing industry for the plants included in the survey. Flares were often used to control intermittent, continuous and emergency VOC emissions. Process boilers, heaters, furnaces and incinerators were also used to varying degrees for these purposes. A general description of these combustion devices is provided in the NO_x/VOC Work Group on Control Technologies report (Federal/Provincial Long Range Transport of Air Pollutants Steering Committee, 1990, Subgroup 6.3, Ch. 2, 6, 10).

(a) Flares

Even though flares are the most widely used devices for controlling chemical plant VOC emissions, there is very little reliable information on the in-use destruction efficiencies, especially for specific chemicals. A comprehensive evaluation of the efficiency of industrial flares conducted in 1985 for the U.S. EPA (Pohl and Soelberg, 1985) indicated that the primary influence on destruction efficiency is flame stability. An Environment Canada study (Geddes and Kotyk, 1987) pointed out that, in addition to destruction efficiency, there are several other important considerations which influence the design and selection of a flare system, including:

- safety and environmental considerations
- volume and composition of gases
- space considerations
- economics.

Neighbourhood concerns should also be considered since flares are generally very visible and noisy.

The complex nature of test procedures for estimating destruction efficiencies precluded the testing of flares under windy conditions in the EPA study. Meteorological conditions encountered may adversely affect the destruction efficiencies of some flare types.

The findings of the EPA study indicate that flares can be operated with destruction efficiencies in excess of 98% to 99%. Operating a flare outside of its stable flame envelope, however, can result in less efficient destruction of VOCs. This is illustrated in Figure IV-1 for several different gases. Combustion efficiency for several flare types is shown inFigure IV-2. The gas exit velocity and heating values were found to have the greatest impact on flame stability. Steam, air or pilot assist can also affect flame stability. Some gases with different heating values but different composition were shown to have different stable flame operating envelopes even when flared from the same flare.

Given the findings of the EPA study, and considering the adverse effects on flaring conditions of wind and variable flow rates and gas compositions, it seems reasonable to assume that destruction efficiencies, at least occasionally, drop below 98%.

It is also evident from the EPA and Environment Canada reports that a great deal of care must be exercised in selecting a flare for the specific conditions under which it will operate. The Environment Canada report is an excellent reference for this purpose.

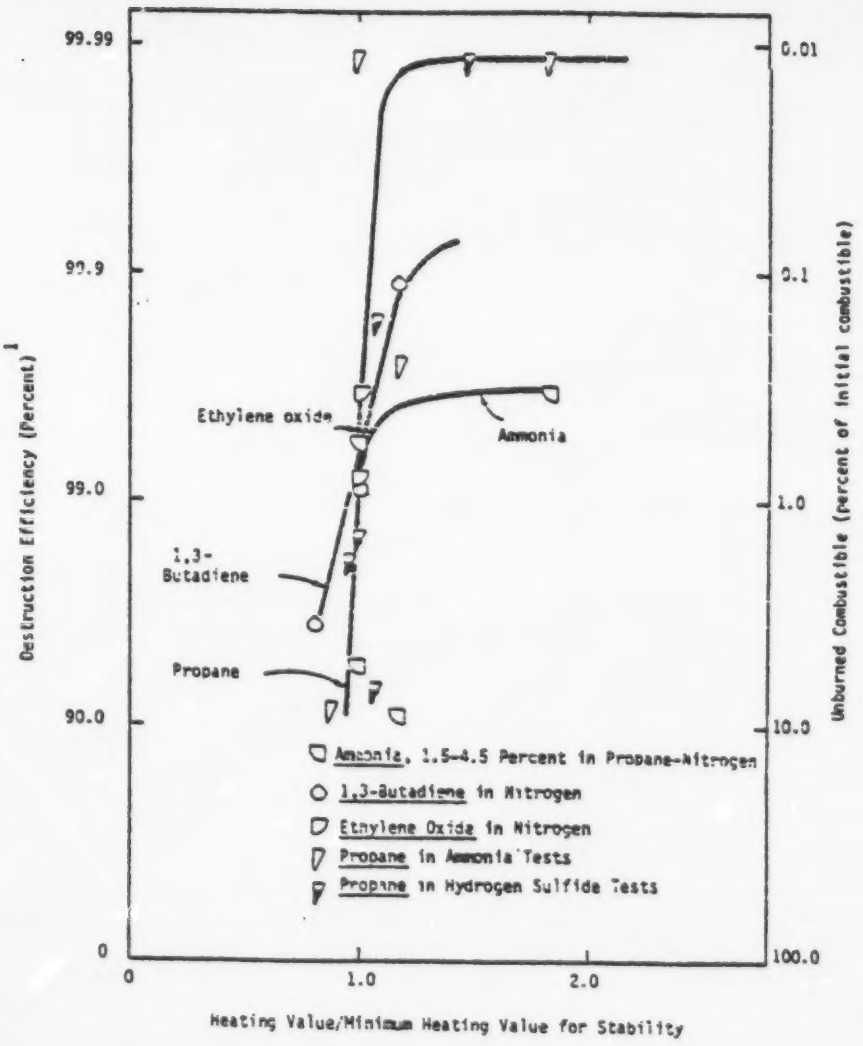


FIGURE IV-1 DESTRUCTION EFFICIENCY OF DIFFERENT GASES

Source: Pohl and Soelberg, 1985

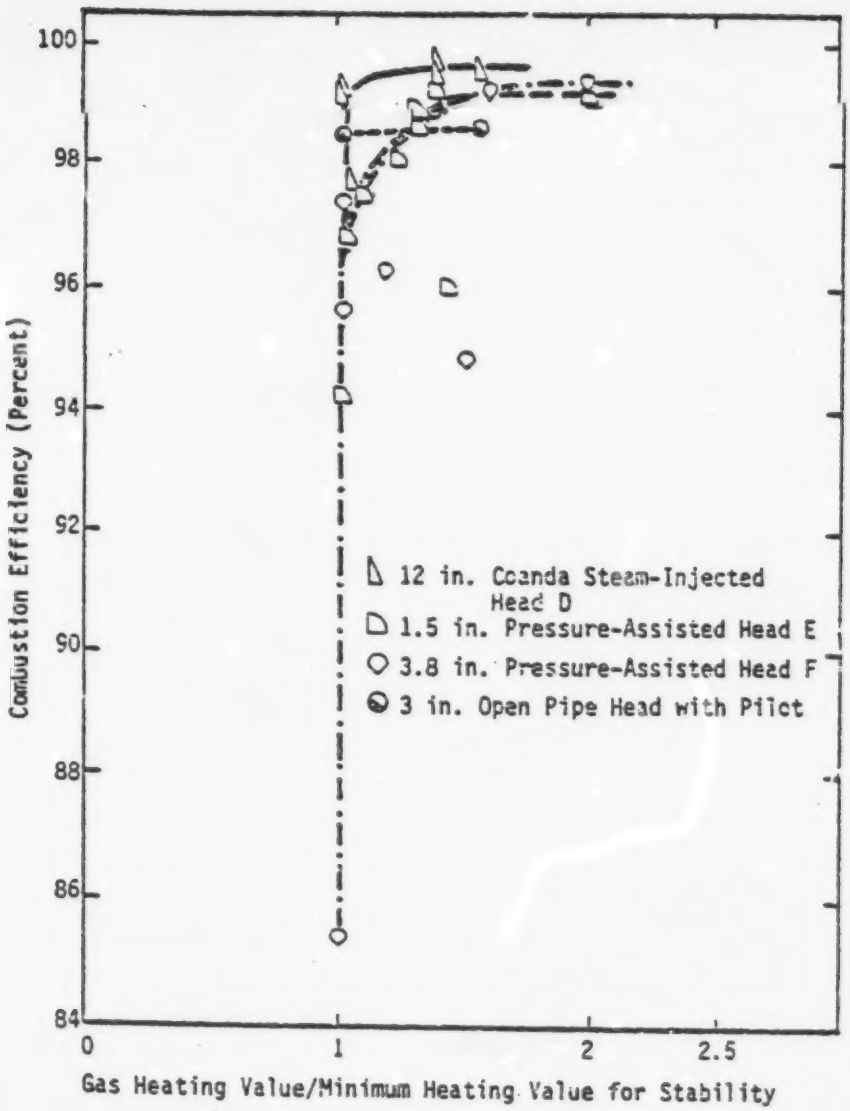


FIGURE IV-2 COMBUSTION EFFICIENCY VS FLAME STABILITY FOR STEAM-INJECTED AND PRESSURE-ASSISTED FLARE HEADS

Source: Pohl and Soelberg, 1985

There are a variety of flare designs available (Table IV-1, Figure IV-3). It is possible to select a system which is suited to the particular conditions of a specific plant. The overall system, because of variability and location of emissions, might include more than one flare or other control device.

The flares reported in use at the surveyed plants were summarized in Table III-16. They are used to control emissions from various sources, including:

- blowdown systems
- storage facility vents
- process vents
- excess fuel gas and intermittent hydrocarbons
- emergency relief valves
- maintenance purging
- fugitive vents (sewers, seal pots, drains)
- compressor oil degassers.

The flares in-use are often downstream of other "control" devices such as degassers and seal pots. Condensors were sometimes used to "concentrate" VOC streams prior to flaring. Installed cost for flare systems easily runs into the millions of dollars because of the header systems, knockout drums, pilot system, assist systems and other related equipment. The flare stacks themselves typically run several hundred thousand dollars. The spread between simple utility flares and staged multi-point flares amounts to a few hundred thousand dollars.

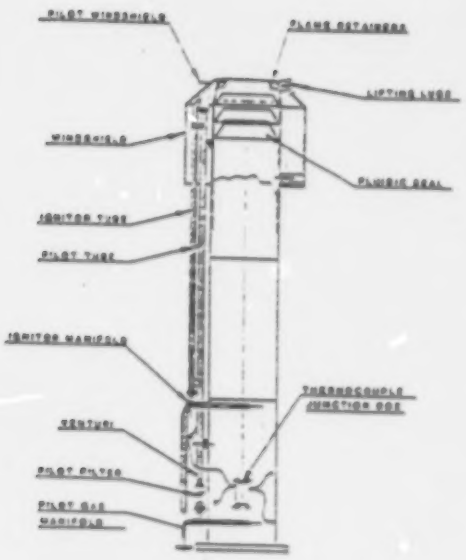
A few costs were obtained from the surveyed companies, but these are very site specific. One company had just spent $ 3,000,000 for a flare and header system to control process vent emissions.

Figures IV-4 and IV-5 illustrate the proportion of operating and capital costs of flare systems and their related components. These capital costs do not include header systems and related piping, but do include site preparation. The cost estimates were developed for a typical large sour gas plant in Alberta for 1987. The purpose of these illustrations is not to report expected costs for similar flare systems in the chemical manufacturing industry. Instead, the purpose is to compare the relative costs of the different flare systems and to compare the proportion of costs from the different components of each system.

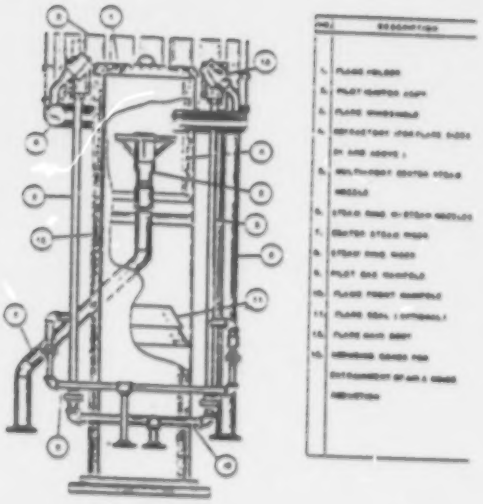
Reduction efficiencies reported by the surveyed companies ranged between 80% and 100%. Most were around 98% to 99+%. Ranges of reduction efficiencies reflecting variable gas flow rates and compositions were also reported. The most extreme range was from 80% to 90%.

TABLE IV-1 SUMMARY OF FLARE TYPES

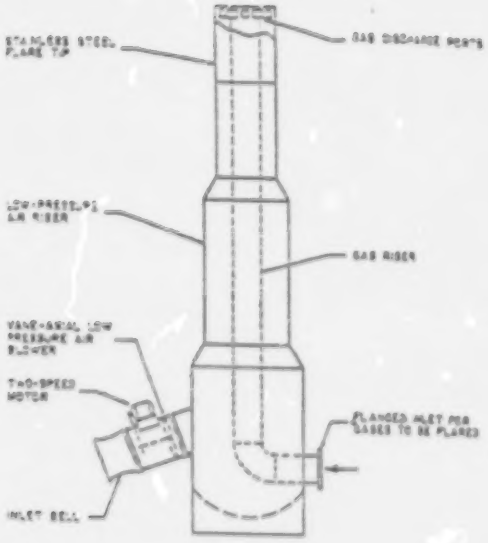
Flare Type	Applications	Comments
Elevated Flares		
Utility Flares	For gases which do not smoke or where there is no smokeless requirement.	Majority of flares now in use.
Steam-Assisted Flares	To prevent smoking.	Steam to flared gas mass ratios typically between 0.15 : 1 and 0.5 : 1.
Water-Assisted Flares	To control smoking.	Freezing problems eliminate its use in Canada.
High-Pressure Gas-Assisted Flares	To control smoking.	At 690 kPag, the ratio of power gas to flare gas is 1 : 3.
Low-Pressure Air-Assisted Flares	To control smoking. Wind has less effect on the flare.	Requires less than stoichometric air for smokeless operation • olefins 0.4 • paraffins 0.3
Staged Multi-Point Flares	For controlling smoking from higher pressure sources.	Minimum pressure drop across flare tip is 34 kPag. 69 kPag is preferable. Can handle a range of flow rates with one flare.
Ground Flares		
Open Ground Flares	Not suitable to flare sour or toxic gases.	
Enclosed Ground Flares	For flows less than 45 - 90 tonnes/hour.	



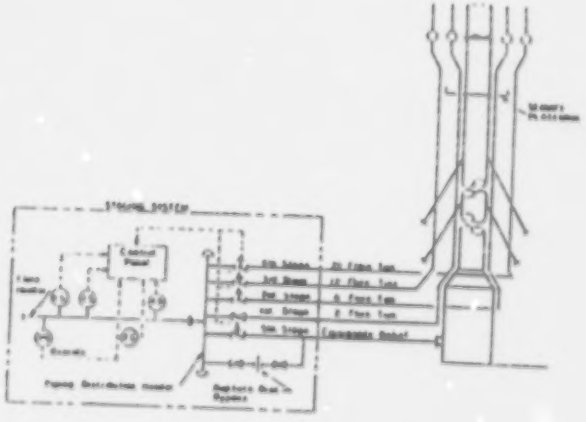
Typical Utility Flare Tip



Typical Steam Assisted Flare Tip



Typical Low Pressure Air Assisted Flare

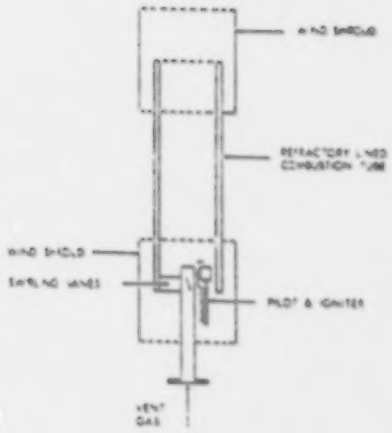


Typical Staged Flake System

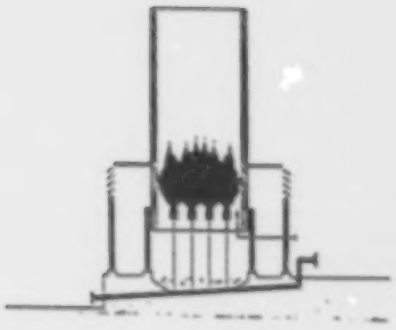
FIGURE IV-3 SCHEMATICS OF A VARIETY OF FLARE TYPES

Source: Geddes and Kotyk, 1987

Typical Open Multi-Point Ground Flare



Waste Gas Incinerator



Typical Enclosed Ground Flare

FIGURE IV-3 SCHEMATICS OF A VARIETY OF FLARE TYPES (CONTINUED)

Source: Geddes and Kotyk, 1987

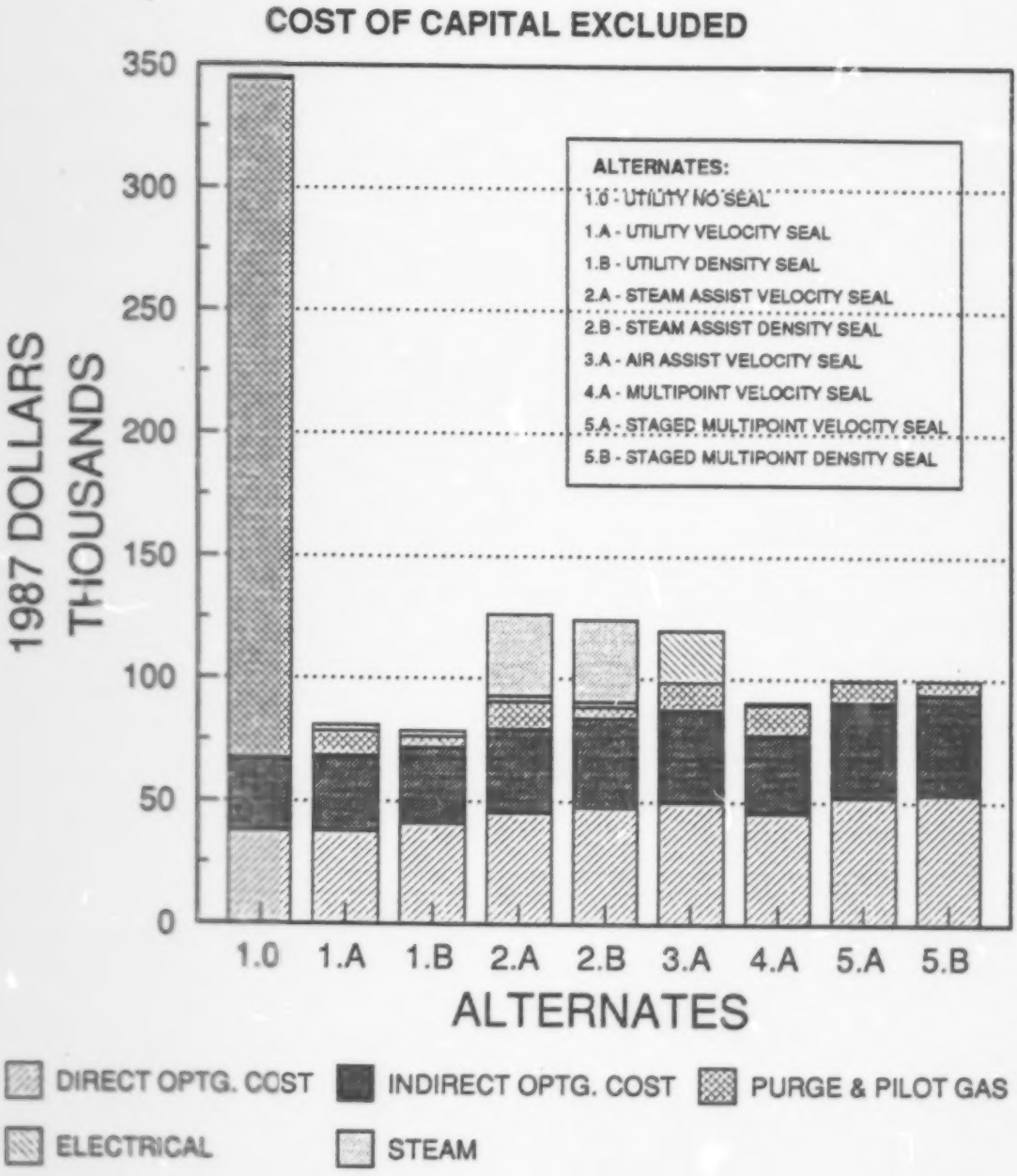


FIGURE IV-4 OPERATING COSTS FOR A VARIETY OF FLARE TYPES

Source: Geddes and Kotyk, 1987

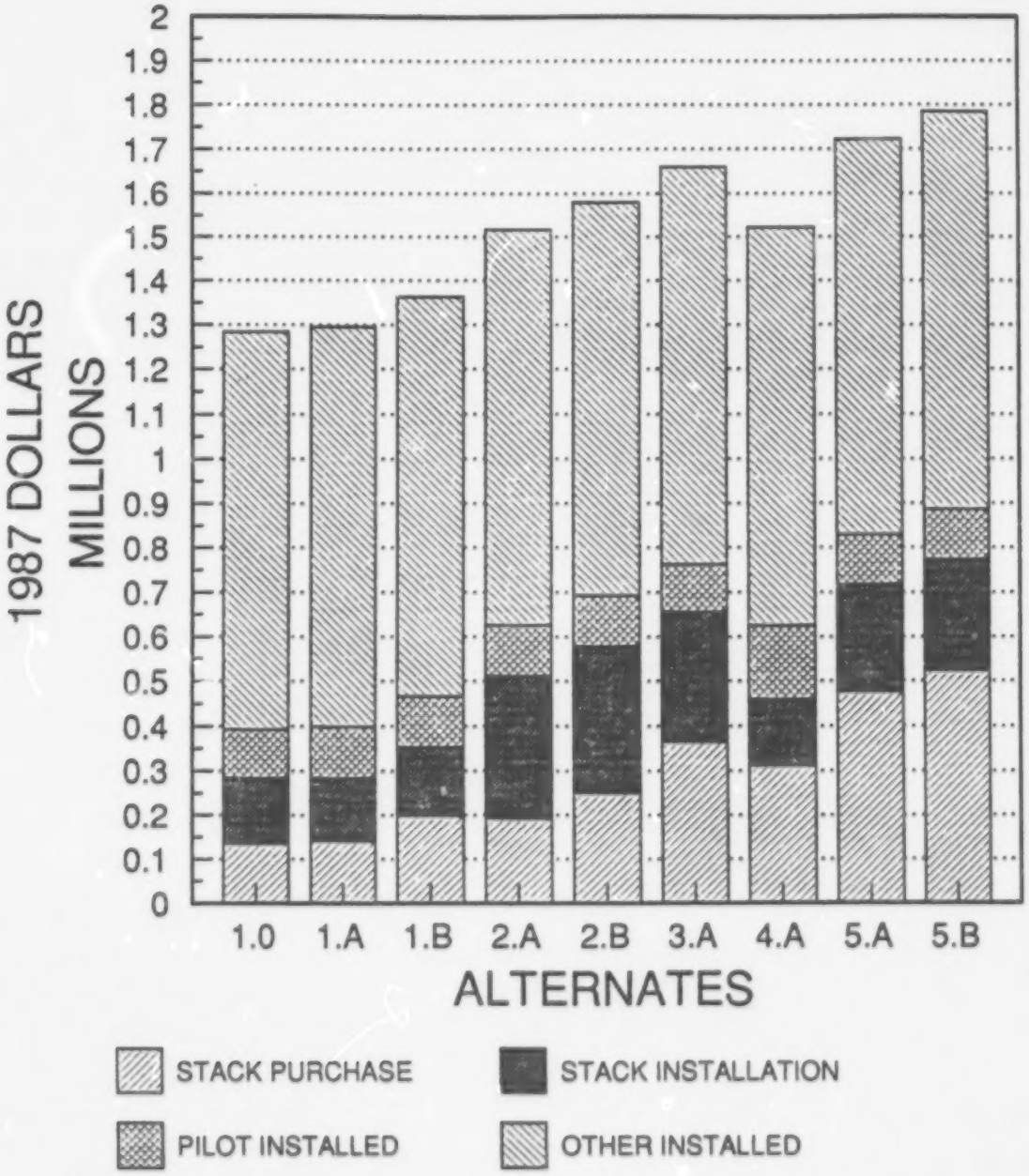


FIGURE IV-5 CAPITAL COSTS FOR A VARIETY OF FLARE TYPES

Adapted from: Geddes and Kotyk, 1987

(b) Incinerators

(i) Catalytic Oxidation

Typically catalytic incinerators can achieve greater than 95% destruction efficiencies when used to treat VOC streams of 50 to 10,000 ppmv, at concentrations less than 25% of the lower explosive limit (LEL) and for flow rates of less than 3,000 Nm^3/min (Kususko and Nunez, 1990). They have been used in numerous applications including printing operations, groundwater stripping and latex monomer production. A typical process flow sketch is shown in Figure IV-6.

Catalytic incinerators have the advantages of lower energy requirements (if make-up gas is needed for low heating value gases) and reduced NO_x emissions because of lower incinerator temperatures (typically less than 400°C in the inlet and less than 700°C in the outlet).

Their main disadvantages are their large volume and catalyst requirements, especially if high destruction efficiencies (> 95% to 98%) are required. Catalyst poisoning is also a serious concern. Typical inhibitory or poisonous materials include phosphorus, sulfur, halogens and various heavy metals. Process fluctuations must also be kept to a minimum. Liquids or solids which could coat the catalyst must be removed. Under normal operating conditions, the useful life of the catalyst is 3 to 5 years.

None of the plants included in the survey reported the use of catalytic oxidation as a means of VOC control.

(ii) Thermal Incinerators

Thermal incinerators can be used to reduce emissions from continuous, and to a lesser extent, intermittent VOC sources. Incinerators are commonly used in the chemical manufacturing industry. They are often used when the VOC destruction efficiency must be very high for control of gases which pose a health risk, or when it is desirable to recover energy from a waste stream.

The key factors which determine destruction efficiency and, hence, the design of thermal incinerators, include:

- temperature
- residence time
- oxygen availability

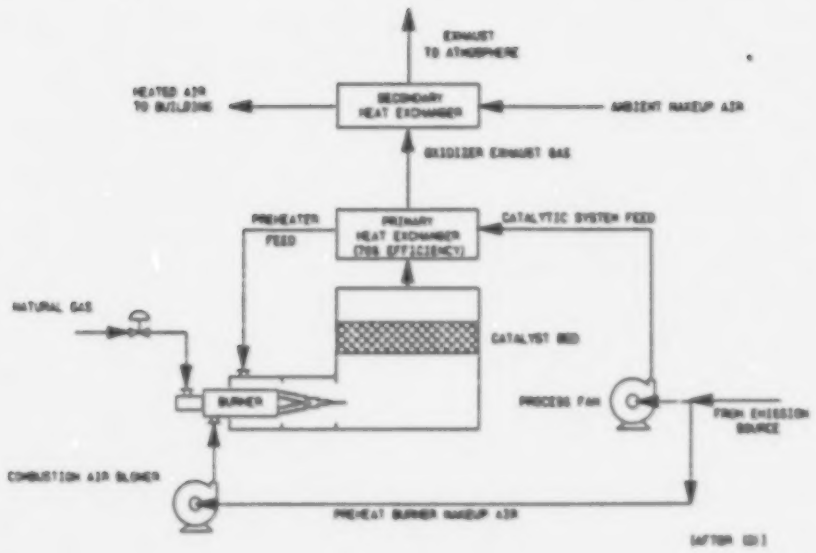


FIGURE IV-6 PROCESS FLOW SKETCH - CATALYTIC OXIDATION SYSTEM

Source: Kosusko and Nanez, 1990

- mixing/turbulence
- the compound(s) of concern.

The temperature and residence time needed to achieve 99% destruction of specific VOCs is illustrated in Table IV-2 (Tessitore et al, 1990). An important conclusion from this data is that the destruction efficiency at a given temperature is highly dependent on the chemicals present. Also significant is that a relatively small increase in temperature results in a marked decrease in the retention time required to achieve the same destruction efficiency.

There is a logarithmic relationship between the fraction remaining and retention time for a given temperature, which can be expressed as:

$$\ln \frac{C_t}{C} = kt_T = A^{(-E/RT)}\, t_T$$

where

C_t = concentration at time t_T
C = initial concentration
A = Arrhenius pre-exponent frequency factor
E = energy of activation (kcal/mole)
R = universal gas constant (1.987 kcal/mole K)
T = absolute temperature (K)
t_T = time required to reach final concentration of C_t

Once the values of A and E are calculated for specific compounds, the equation can be used to estimate the destruction characteristics of a compound at any given temperature and retention time combination.

The effects of oxygen on destruction efficiency is clearly illustrated in Figure IV-7 and IV-8 for toluene and benzene, respectively. Similar curves can be generated for most compounds. Good mixing is very important to provide heat transfer and oxygen and to prevent stratification and escape of undestructed organics.

Incinerators are clearly more controllable than flares, but tend to be of higher cost. When the total costs, including tie-in and capture, less credits for energy recovery, if applicable, are considered, an incinerator may be justified if it is important to ensure very high destruction efficiencies (> 99%). This might be the case if toxic or hazardous gases are handled. Some of the surveyed companies use incinerators instead of flares for this reason.

TABLE IV-2 THERMAL DESTRUCTION TEMPERATURES TO ACHIEVE 99% DESTRUCTION EFFICIENCY (TEMPERATURE °C)

Compound	Retention Time		
	0.5 Sec	1.0 Sec	2.0 Sec
Benzene	836	793	754
Toluene	744	726	707
Xylenes	1181	1144	1109
Ethylene*	804	773	744
Propylene*			
Styrene*			

* Temperature for destruction efficiency of limiting compound (carbon tetrachloride)

Source: Tessitore et al, 1990

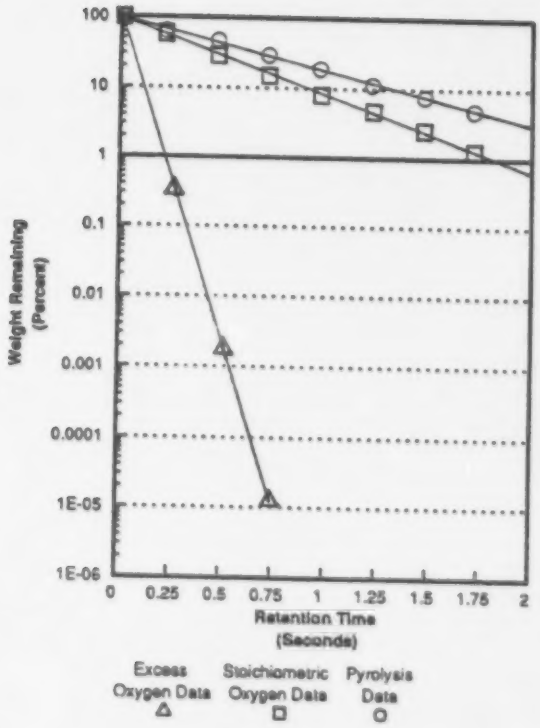


FIGURE IV-7 PERCENT WEIGHT OF TOLUENE REMAINING AFTER THERMAL OXIDATION AT 760°C

Adapted from: Tessitore et al, 1990

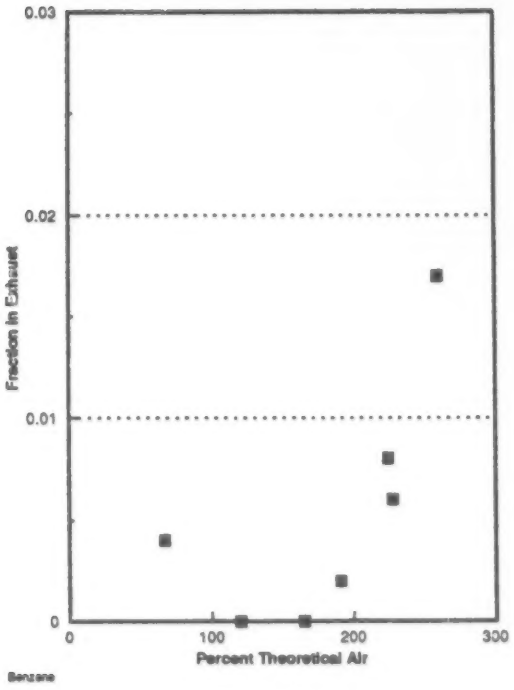


FIGURE IV-8 EFFECTS OF EXCESS AIR/OXYGEN ON THERMAL DESTRUCTION OF ORGANIC COMPOUNDS (BENZENE)

Adapted from: Tessitore et al, 1990

(c) Boilers/Heaters/Furnaces

Process boilers, heaters or furnaces can often provide capacity for VOC destruction. They have several advantages over flares, including:

- reduced capital requirements (already existing or needed for other purposes)
- energy recovery from higher heating value VOC streams
- can handle dilute (low heating value) VOC streams, such as ventilation air, sewer sump units, etc., because the primary fuel provides combustion stability.

Disadvantages include:

- likely not suitable for intermittent or emergency VOC releases
- may not be able to handle the required gas volume
- increases the complexity of boiler/heater/furnace operation
- require regular maintenance, resulting in reduced availability
- alternate control is needed when the system is not available.

The typically long retention times provide excellent VOC destruction efficiencies. Depending on the design of the boilers, heaters or furnaces, NO_x emissions may also be lower than if the gases were flared.

Boilers, heaters and furnaces were used in the surveyed companies to control process vent streams, purge streams and waste gas streams.

Some of the limitations which may restrict expanded use of boilers, heaters and furnaces for VOC control include:

- volume of gas should not adversely affect the operation of the combustion system
- waste gas must not damage the process burner internals
- the burner should be near the waste gas source.

Five of the surveyed plants reported the use of boilers, heaters or furnaces as a means of VOC control.

2. Condensation

Condensation is a widely used method of controlling VOC emissions from process streams. Condensers are sometimes an integral part of a process, used to separate or recover products. Other condensers are strictly used to capture VOC emissions for recirculation back to the process or to fuel gas uses.

There are a variety of configurations and condenser types available. Two general categories are air- or liquid-cooled condensers and refrigerated condensers. The former type can be quite effective for high temperature streams when available fluids, typically water or air, can provide sufficient temperature differentials. Refrigerated condensers are typically more costly, especially when used to cool significantly below 0°C. Two-stage systems are usually required when cooling below 0°C, the first stage to remove water just above 0°C.

Condensers are suitable for controlling VOC emissions when the gas streams have low vapour pressures. Gas streams with high vapour pressures (> 40 - 60 kPa) or high inert concentrations cannot effectively be controlled by condensers (Hall, 1990). Reduction efficiencies would be low or refrigeration requirements would be excessive. Consequently, condensors are often found on distillation column vents and other process vents which have low inerts.

In exothermic reactions, reactor temperatures can be partially controlled by condensing overhead vapours and returning the recovered liquid back to the reactor. Here the condenser serves to cool the process reactor and recovers hydrocarbons at the same time.

Two-stage condensers or two condensers in series, such as a water-cooled condenser followed by a refrigerated condenser are commonly used. There are also a variety of techniques developed to get around freezing problems in gas streams with high dew points.

Recent cost quotations for a 600 hp refrigeration unit designed to operate at -25°C and handling a gas flow rate of about 20,000 m^3/h with 1100 kg/h of hydrocarbons was $ 1.5 x 10^6. Installation costs and tie-ins were extra. This was designed for a relatively rich aromatics stream. The company anticipated that a carbon bed would be required as a polishing unit following refrigeration at -25°C. Alternatively, the refrigeration unit would have to be sized to operate at about -60°C. Reduction efficiencies at the -60°C operating temperature were anticipated to be sufficient to meet regulatory discharge emission limits.

Another application of condensers is on storage tank or product transfer stations. Here concentrations are high and flow rates are low. A schematic of a typical system is shown in Figure IV-9. Additional information about condensation processes is available from the U.S. EPA (Basdekis et al, 1980).

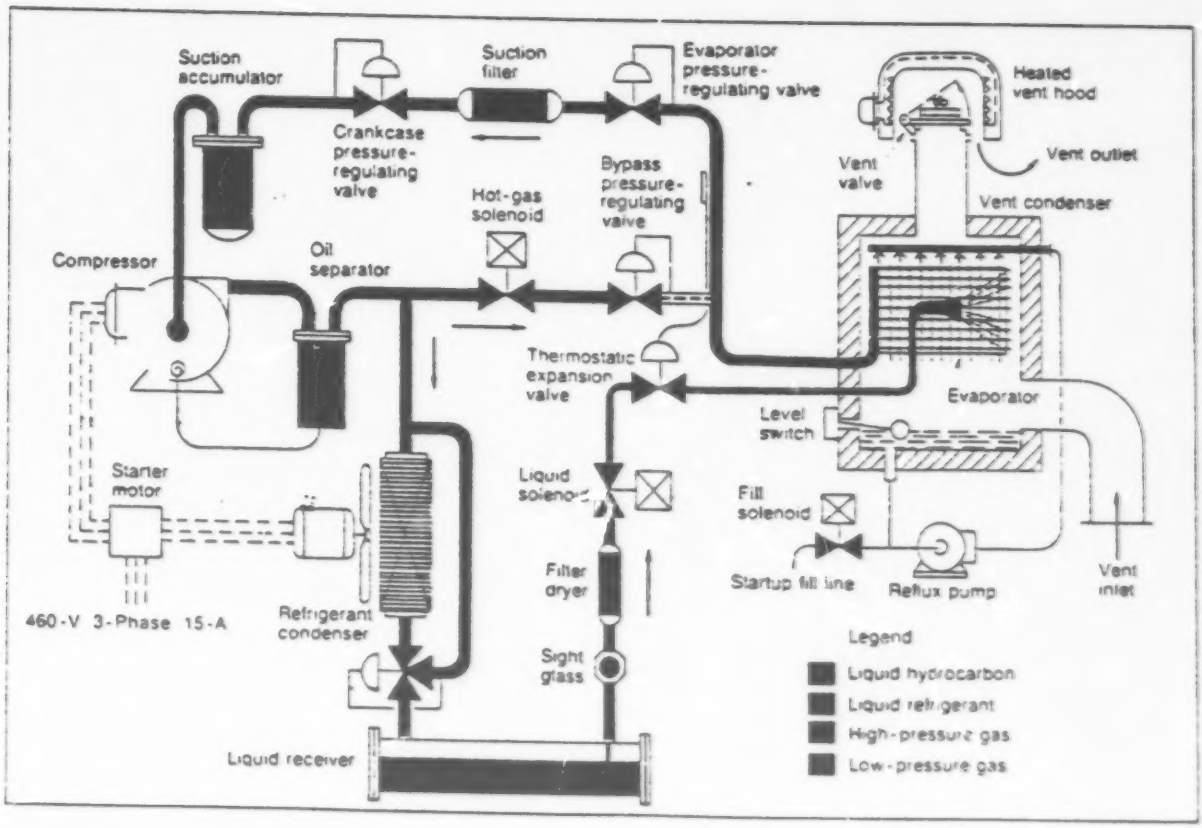


FIGURE IV-9 TYPICAL REFRIGERATED VAPOUR-RECOVERY SYSTEM FOR A STORAGE TANK OR PRODUCT TRANSFER STATION

Source: Forrester and LeBlanc, 1988

3. Adsorption

Adsorption refers to the physical phenomenon wherein vapour molecules are adsorbed on a solid or liquid surface. Where adsorption is accompanied by chemical reaction, the process is termed, "Chemsorption", an exothermic process where molecules can be only one layer thick. This process has little application for organic solvent control.

When adsorption does not involve chemical reaction, the process is termed physical adsorption. The process is reversible and vapour molecules can be adsorbed in more than one layer. Note that some adsorbents (activated carbon) catalyze hydrolysis and breakdown reactions of some solvents, such as ketones.

Activated carbon is the only physical adsorbent presently in widespread use for organic vapours. Other adsorbents could be used (activated alumina, etc.) but experience has shown that carbon is most suitable.

The capacity of activated carbon to pick up organic vapour is shown by adsorption isotherms, such as in Figure IV-10 showing the effect of molecular weight on carbon capacity. For pollution control the range of interest is below 10 mm of mercury pressure.

The Polanyi equation can be used to predict the effect of inlet pollutant concentration on adsorption capacity where the inlet concentration is low:

$$\text{Adsorption capacity } \frac{\text{g hydrocarbon}}{\text{g carbon}} = \frac{V_m}{T \log \frac{C_o}{C_i}}$$

V_m = molar volume of organic vapour
T = absolute temperature
C_o = concentration of saturated vapour
C_i = initial vapour concentration into adsorber

For a fixed bed carbon adsorber the concentration profile in the bed changes as the capacity of the bed is reached. Figure IV-11 shows such profiles for a hypothetical solvent.

For exhaust streams containing multiple solvents, components of higher molecular weight will displace those with lower molecular weight. Thus the component with the lowest molecular weight will leave the carbon first.

Activated carbon is typically regenerated either by heating with steam, hot air or a hot inert gas, or by drawing a vacuum. Regeneration with steam is the most widely used technique. During regeneration the eluting gas and solvent come off

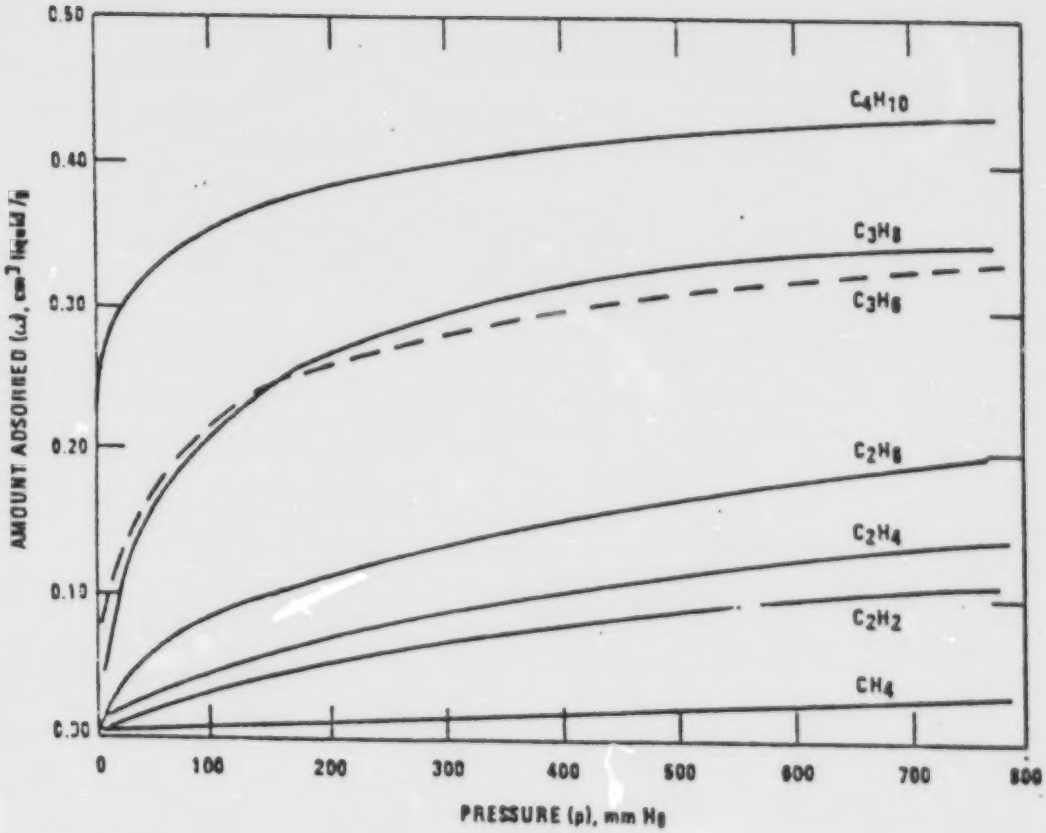


FIGURE IV-10 ADSORPTION ISOTHERMS OF HYDROCARBON VAPOURS[a]

[a] Temperature = 100°F (38°C)

Source: B.H. Levelton & Associates Ltd., 1979

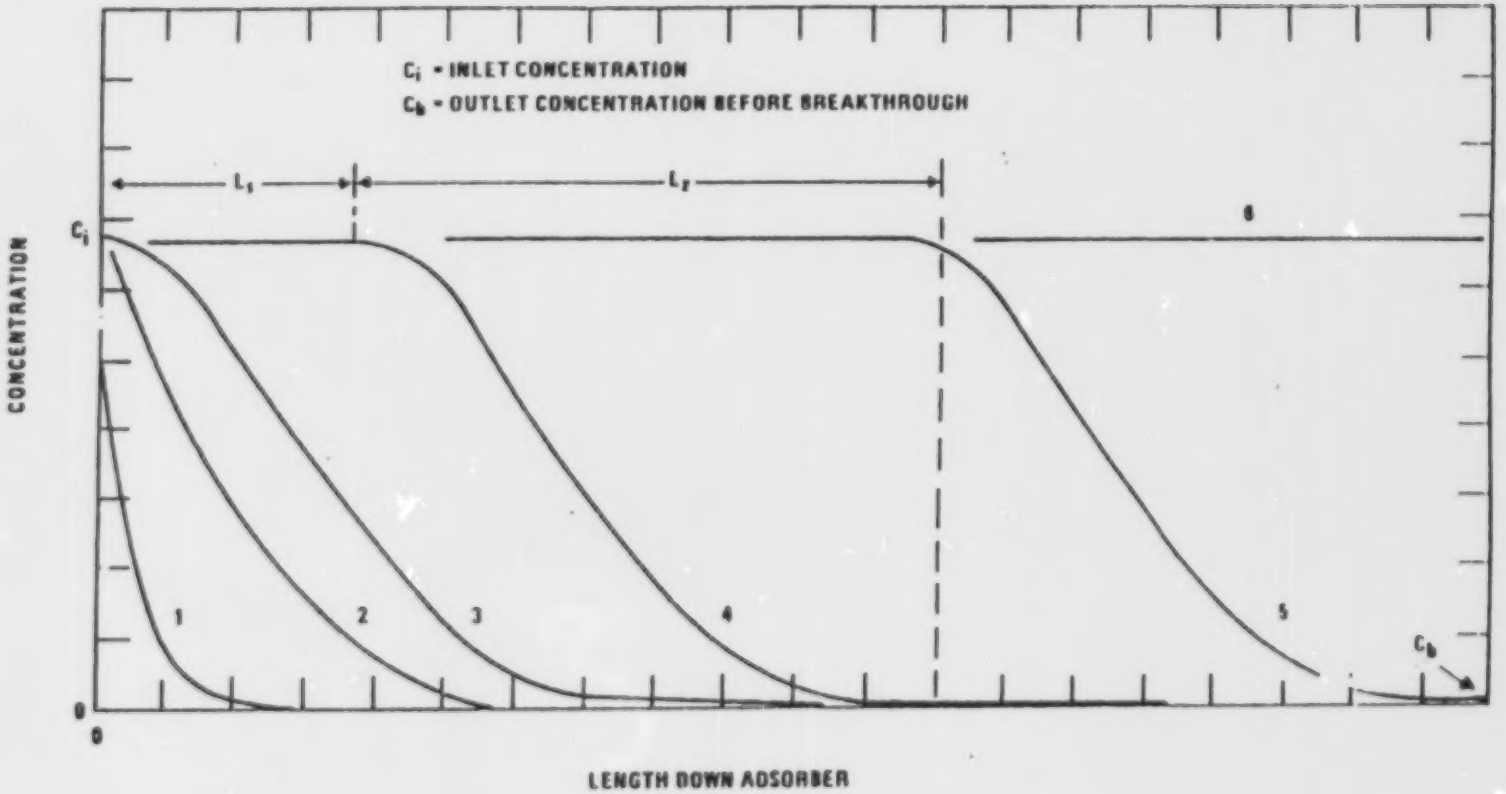


FIGURE IV-11 MOVEMENT OF VAPOUR CONCENTRATION DISTRIBUTION CURVE IN CARBON BED WITH INCREASED ADSORPTION TIME

Source: B.H. Levelton & Associates Ltd., 1979

together. This stream can be incinerated or condensed, depending on whether or not vapour recovery is desired. It is not practical to try to remove all organic vapour from the carbon during regeneration.

Problems which arise in carbon adsorption are:

- Thermal breakdown of solvents and resins during oven curing may lead to compounds which cannot be adequately adsorbed. Polymerization reactions lead to tars which may foul the activated carbon.
- Ketone and phenol cause problems because of high heat of adsorption.
- Recovery of mixed organic vapours for re-use does not appear to be feasible and the vapours may have only fuel value.
- Particulate matter coats and plugs the bed.
- Carbon capacity is highest at low temperature (38°C maximum is normal) so gases should be cooled.
- Water vapour competes with solvent for adsorption sites, hence, relative humidity should be below 50 percent.
- The range of concentrations for which carbon adsorption is applicable is limited. Operating costs are high at low concentrations and the bed heats by exothermic adsorption at higher levels of vapour concentration.

One of the surveyed chemical manufacturers recently replaced two sets of twin-carbon beds used to recover toluene and benzene from phenol and benzoic acid production units, with a larger set of twin carbon beds. Off-gas from the phenol and benzoic acid reactors are tied into the carbon beds. Provisions for tying-in tank vents, other process vents and a variety of fugitive sources, both intermittent and continuous, were also designed into the system.

Off-gas from the air-blown reactors is passed through refrigerated condensers to remove water and some hydrocarbons. This reduces the loading and, hence, the size of the carbon beds.

The total cost for a twin bed carbon adsorption system installed in 1989 with steam regeneration was about $ 2.2 million. This system was conservatively designed for a 23,000 m^3/h gas flow rate and a hydrocarbon content of over 1100 kg/h. The gas composition is 86% N_2 with approximately equal parts of O_2 and CO_2 making up the remainder. The delivered cost of the carbon beds, including about $ 200,000 for carbon, was about $ 1.0 million. The additional costs were for:

- vapour line extensions
- base
- air to gas cooler for summer operation
- receiving tank
- API separator
- control and monitoring equipment
- erection labour.

The system included automatic sampling with alarms, as well as a closed loop air cooling cycle which uses off-gas from the adsorbing bed to cool the regenerated bed. This was made possible by enlarging the steam condenser which is used for capturing the steam/hydrocarbon mixture emitted during regeneration.

Operating costs have been minimal because of automation. The operator expects maintenance costs to be about 5% of capital or about $ 50,000/yr on average. The system uses about 3500 kg/h of steam on a daily average. The bed life is expected to be in excess of 5 years. A similar bed operated for 12 years with only some re-sieving and partial carbon replacement.

Hydrocarbon reduction efficiencies have been estimated at 99.8%. Emissions are typically below 5 ppm. The carbon adsorption system in the above plant is an integral part of the process. Bypassing of the system would mean losing too much chemical. The operator estimated that the incremental reductions in hydrocarbons after replacing the smaller carbon adsorption system with the new system would only pay for a portion of the operating costs. The operator also investigated condensation, absorption and incineration systems in detail and concluded that, for their particular application, the four systems were comparable in cost.

4. Absorption

Absorption (scrubbing) involves dissolving a soluble gas component in a relatively non-volatile liquid. The absorption is only the collection step. After the gas is dissolved, it must be recovered or disposed.

The absorption regeneration technique is limited by low concentrations and low solubilities of most organic gases in the absorbent.

Absorption in the chemical manufacturing industry would most likely take place in packed or tray towers. These systems are described in more detail in the U.S. EPA report of control devices for the organic chemical manufacturing industry (Basdekis et al, 1980). Each has its advantages and disadvantages. In general, packed towers are favoured economically for diameters less than 0.6 m and plate tray towers are favoured economically for diameters greater than 1.2 m.

A key parameter in absorbers is that the gas must be very soluble in the solvent. The solvent must have other properties, such as:

- low vapour pressure
- low viscosity
- low cost
- preferably non-corrosive
- non-toxic
- non-flammable
- chemically stable
- low freezing point.

Water is a common solvent because of its unique properties. It is often used on a once-through basis with or without stripping. Significant secondary emissions may result from such a design.

Recirculation of solvents tends to increase capital costs for the absorbing tower, because of reduced absorption efficiencies compared to once-through systems. Stripping and heat exchanging equipment requirements may also be higher when recirculating solvents.

The design of absorbing systems and, hence, the costs are very dependent on the vapour equilibrium properties of the particular VOC-solvent system.

Scrubbing is commonly used in the chemical manufacturing industry to control VOC emissions from tanks.

There are examples of oil absorption systems in the U.S. that are used to recover aromatics. One system operated for over 10 years with no significant problems. Reduction efficiencies of 95% to 98% were achieved. The absorbed aromatics were recovered from the absorbing fluid by distillation.

Four scrubbers were reported in use by the surveyed plants to control emissions from tanks and loading operations.

5. Process and Equipment Modifications

There are some process and equipment modifications which can be made to facilitate the reduction of VOC emissions.

The use of surface condensers instead of barometric condensers to cool gas streams will eliminate contaminated water and the resultant emissions from sewers and holding or treating ponds. This practice is already widespread. It is a very sensible conversion to undertake because of reductions in water effluent contamination and reductions in emissions if the condensed hydrocarbons are recirculated to the process or sent to some VOC control device.

Vacuum systems are commonly used in the manufacture of some organic chemicals. The amount of material in a gaseous state is related to the chemical

component vapour pressures and the system operating pressure. Operating at a lower pressure (i.e. drawing a higher vacuum) means more material in a vapourized state. Oversizing of vacuum pumps then potentially leads to increased VOC emissions because of lower operating pressures.

Vacuum pumps are sometimes over-designed and then operated with an air bleed to reduce the working vacuum achieved. The fresh air creates a driving force for liquids to vapourize, thus leading to potentially higher VOC emissions. This can be controlled by bleeding in the vacuum pump exhaust instead of fresh air.

Vacuum pumps typically use water or other liquids to provide a seal. The sealant can either be flushed through the vacuum pump (for water sealant) or it can be recirculated through a small seal tank (water or other liquid sealant). Since the sealant will absorb some of the soluble hydrocarbons, its discharge will result in VOC emissions and possible water treatment requirements. The use of a seal tank facilitates the capture of these hydrocarbons.

Gas-sealed vacuum pumps have the potential to reduce VOC emissions from vacuum operations. In these pumps, gases do not contact seal fluids. However, gas-sealed pumps are not often selected for use in vacuum applications in the chemical manufacturing industry.

Inert gas blankets, used to prevent chemical decomposition or to prevent a process from operating in the explosive range, carry away hydrocarbons. Higher operating temperatures and pressures radically increase the inert gas requirements, resulting in increased VOC emissions.

Quench tower water can be recirculated back to the quench tower if it is first cooled in heat exchangers. This reduces the load of contaminated water on the treatment process as well as reducing the amount of hydrocarbon absorbed in the quench water.

Another process modification is to use recycle compressors. In some plants such compressors are used on the gas that would normally be flared and return the gas to the process. For example, BTX plants mentioned they use this technique. Another example is a compressor for the stripper steam vent in ethylene oxide plants which may be compressed and recycled to the carbon dioxide absorber. Some ethylene from naphtha plants employ a recycle compressor for the compressor lube oil vent. This vent gas is returned to the charge gas compressor suction.

Closed-loop drying systems have been mentioned as a necessary change for some processes. For example, in the solution process for polyethylene, some plants may use air for drying product which is ultimately discharged to the atmosphere. Such systems have been replaced with closed-loop systems. Some of the systems use nitrogen rather than air.

Some processes, such as polyethylene plants, have added material recovery process sections. The primary purpose of these process units is to reduce losses and VOC emissions. Polyethylene plants in the U.S. have been encouraged to reduce the amount of dilution air used in their VOC containing ventilation and process air.

B. Control of Fugitive Emissions

1. Inspection and Repair Programs

The sources of fugitive emissions include:

- pumps
- compressors
- process valves
- safety relief devices
- agitators
- open-ended lines
- sampling connections
- flanges
- sewers
- cooling towers
- treatment ponds.

Most of these sources are described in more detail in the NO_x/VOC Work Group on Control Technologies report.

Most fugitive emission reduction programs involve quarterly or even monthly inspection. The objective is to identify leaking equipment. Visual, olfactory, audible or instrument techniques can be used to detect sources of fugitive VOC emissions. The fugitive emission inspection methods include:

- individual component surveys (a part of all methods)
- area of walk-through surveys
- fixed point monitoring.

Visual methods are good for detecting liquid leaks but this may not indicate a VOC emission, depending on the fluid. High pressure leaks can often be heard, while other leaks can sometimes be detected by their odour. Visual methods are often not sensitive enough to detect most leaks.

Soapy solutions can enhance leak detection capability. Soap solutions, however, do not distinguish between VOC and non-VOC emissions, can only be used qualitatively, and are not suited to hot equipment nor rotating equipment. Ultrasonic detectors can be used qualitatively for high pressure leaks.

Portable hydrocarbon analyzers are used to provide quantitative leak detection of VOC emissions. The U.S. EPA recommends using methane as the reference gas at a concentration of 10,000 ppmv for measurement of leaks at the surface of the equipment (Goodwin, 1980). Method 21 defines a procedure for detecting fugitive VOC emissions.

In the United States, a VOC concentration at a leak of 10,000 ppmv is usually considered an action level for repair/maintenance. This is considered representative of reasonably available control technology (RACT). Large mass emission rate variations may occur over short time periods for individual components.

Less costly methods than a survey of individual components are desirable. Alternative techniques include walking through areas with a hydrocarbon analyzer or placing several analyzers in fixed locations. These methods have estimated chances of detecting large leaks of 50% and 33%, respectively (Goodwin, 1980). Once a leak is suspected in an area, an individual component survey is required to pinpoint the source of the leak.

Tightening of packing or seals, flanges, etc. while the leaking equipment is in service can sometimes reduce VOC emissions. Other times, however, the packing or seals have already been tightened to their limit or they are worn or dried in which case tightening can even lead to increased VOC emissions.

When in-service adjustments cannot be made, the leaking equipment must be isolated and taken out of service. This can result in substantial VOC emissions because of flushing out lines or draining equipment. Consequently, it may be more prudent to monitor a small leak and wait for a plant turnaround to repair or replace the leaking equipment.

It may be possible to seal leaking process valves by injecting a sealing fluid into the source. This has been successfully used in the petroleum industry in California (Goodwin, 1980). The operability of the valve may be affected by the sealant, therefore, this method may be limited to short-term applications.

The control efficiency of inspection and repair programs ranges from 40% to 70% and 50% to 80% for quarterly and monthly programs, respectively. The efficiency is affected by several factors including:

- action level
- inspection frequency
- achievable emission reduction
- delay between detection and repair of the leak.

Table IV-3 illustrates the effect of action level on the fraction of total VOC mass emissions. The type of fluid has a significant effect on the selection of an action level.

TABLE IV-3 FRACTION OF TOTAL MASS EMISSIONS FROM VARIOUS SOURCE TYPES THAT WOULD BE AFFECTED BY DIFFERENT ACTION LEVELS[a]

Action Level[b] (ppmv)	Fraction of Mass Emissions (as %)			
	100,000	50,000	10,000	1,000
Source Type				
Pump Seals				
Light liquid service	56	68	87	97
Heavy liquid service	0	0	21	66
In-Line Valves				
Vapour service	85	92	98	99
Light liquid service	49	62	84	96
Heavy liquid service	0	0	0	23
Safety/Relief Valves	20	33	69	92
Compressor Seals	28	48	84	98
Flanges	0	0	0	48

[a] These data show the fraction of the total emissions from a given source type that is attributable to sources with leaks above the various action levels.

[b] Level of emission at which repair of the source is required.

Source: Goodwin, 1980

Table IV-4 illustrates the effect of inspection frequency on leak detection.

Table IV-5 illustrates the achievable emission reduction assuming a leak of 10,000 ppmv could be reduced to 1000 ppmv. Repairs of leaks less than or equal to 1000 ppmv may not result in any significant emission reductions.

Nine of the fourteen surveyed plants submitted information about control measures undertaken to reduce fugitive emissions. Eight plants were using formal inspection and maintenance programs, of varying degrees of complexity, and the remaining plants were all planning to implement programs. Typically, the approach involves use of a hydrocarbon analyzer by one or more employees on a part-time or full-time basis to check for leaks. Initially, repairs would be done by the plant's regular maintenance staff. No new staff would be added until the work load was established.

One company was planning to tag leaking equipment with different coloured flagging to indicate leaks over and under 10,000 ppmv. Major leakers would get the immediate attention of maintenance. Minor leakers would be monitored more frequently and repaired on a lower priority basis, depending on work load.

A listing of current practices for fugitive emission control is given in Appendix B.

Estimates of resources allocated to the inspection and repair program ranged from 1/3 to 1 man-year per unit initially. This assumed the additional repair work could be accommodated in the maintenance schedules.

Other alternatives to the leak detection and repair programs have been proposed (Berglund, 1990 and Berglund et al, 1990). The alternative program suggests an initial screening of all affected components as a classifying exercise. Equipment would then be classified as acceptable or as questionable. Acceptable equipment would be monitored at a greatly reduced frequency and only to provide a statistical sampling. Questionable equipment would be monitored quarterly until the leaking equipment is corrected, repaired or replaced.

The proponents to this alternative feel that this system allows more effort to be spent on problem components, while maintaining a watch on the acceptable components. More can be accomplished for the same level of effort or less.

In the U.S., a survey of ethylene oxide plants confirmed these to be relatively low fugitive emitters (Berglund et al, 1990). The following specific programs were cited as influencing this record, including:

- installation of gas detectors at strategic plant locations with regular sample analyzers;

TABLE IV-4 ESTIMATED OCCURRENCE AND RECURRENCE RATE OF LEAKS FOR VARIOUS MONITORING INTERVALS

Source Type	Estimated Percent of Sources Leaking at Above 10,000 ppm Initially[a]	Estimated Percent of Initial Leaks Which are Found Leaking at Subsequent Inspections[b]			Estimated Percent of Sources Which are Found Leaking at Subsequent Inspections[c]		
		Annual	Quarterly	Monthly	Annual	Quarterly	Monthly
Pump seals							
Light liquid service	23	20	10	5	4.6	2.3	1.2
Heavy liquid service	2	20	10	5	0.4	0.2	0.1
In-Line valves							
Vapour service	10	20	10	5	2.0	1.0	0.5
Light liquid service	12	20	10	5	2.4	1.2	0.6
Heavy liquid service	0	20	10	5	0.0	0.0	0.0
Safety/relief valves	8	20	10	5	1.6	0.8	0.4
Compressor seals	33	20	10	5	6.3	3.3	1.7
Flanges	0	20	10	5	0.0	0.0	0.0

[a] Approximate fraction of sources having leaks equal to or greater than 10,000 ppm prior to repair.

[b] Approximate fraction of leaking sources that were repaired but found to leak during subsequent inspections. These approximations are based on engineering judgment.

[c] Approximate fraction of sources that were repaired but found to leak during a subsequent inspection. These approximations are the product of the information presented in footnotes a and b.

Source: Goodwin, 1980

TABLE IV-5 AVERAGE EMISSION RATES FROM SOURCES ABOVE 10,000 PPMV AND AT 1000 PPMV

Source Type	(Y) Emission Rate from Sources Above 10,000 ppmv[a] (kg/hr)	(X) Emission Rate from Sources at 1000 ppmv[b] (kg/hr)	$(\frac{Y - X}{Y})$ (100) Percentage Reduction
Pump Seals			
Light liquid service	0.45	0.035	92.0
Heavy liquid service	0.21	0.035	83.0
In-Line valves			
Vapour service	0.21	0.001	99.5
Light liquid service	0.07	0.004	94.0
Heavy liquid service	0.005	0.004	20.0
Safety/relief valves	1.4	0.035	97.5
Compressor seals	1.1	0.035	97.0
Flanges	0.003	0.002	33.0

[a] Average emission rate of all sources, within a source type, having screening values above 10,000 ppmv.

[b] Emission rate of all sources, within a source type, having screening values of 1000 ppmv.

Source: Goodwin, 1980.

- use of double mechanical seals and liquid buffers, equipped with automatic alarms or shutoffs on pumps;
- use of labyrinth shaft seals with pressurized N_2 on compressors;
- use of welded construction instead of flanges were possible;
- use of leak detectors for critical flanges;
- extra maintenance;
- study of vibrating characteristics to anticipate pending problems;
- collection, absorbing in water and discharging to sewer any leakage or drainage from sampling operations and pump vents;
- daily leak inspections by plant personnel;
- immediate leak repair.

2. Replacement of Leaking Equipment with Low or Non-Leaking Equipment

The use of low or non-leaking equipment can significantly reduce VOC emissions, but only in some applications. Reduction efficiencies expected with this equipment are reported in Table IV-6.

Sealless pumps, such as diaphragm pumps, which do not have shaft/casing junctions are often used with toxic or hazardous fluids. Emissions would only occur if a diaphragm was ruptured.

Dual mechanical seals, utilizing a barrier fluid circulating between the seals, can be effective in reducing VOC emissions. In the back-to-back configuration, the barrier fluid is at a higher pressure than the pumped fluid. Seal leaks would result in barrier fluid flowing into the product or out of the outer seal. Where product contamination is a concern, pure product, product additives or diluents might be used. Otherwise, water, steam, glycols, oil, methanol and heat transfer fluids are typically used for barrier fluids.

In tandem seal configurations where the barrier fluid pressure may be lower than the pumped fluid pressure, the barrier fluid could be contaminated in the event of an inner seal leak. Therefore, these systems have degassing vents which can be controlled by closed vent systems. The closed vent systems capture the emissions and redirect them to a VOC control device.

These closed vent systems can also be used for controlling emissions from pump seal areas. Care must be exercised to avoid explosive mixtures.

TABLE IV-6 EFFECTIVENESS OF EQUIPMENT MODIFICATIONS

Source Type/Equipment Modification	Control Efficiency (%)
Pumps	
Sealless pumps	100
Double mechanical seals/closed vent system	~100[a]
Closed vent system on seal area	~100[a]
Compressors	
Double mechanical seals/closed vent system	~100[a]
Closed vent system on seal area	~100[a]
Safety/relief valves	
Closed vent system	60[b]
Rupture disks	100
Open-ended lines	
Caps, plugs, blinds, second valves	100[c]
Sampling connections	
Closed loop sampling	100
In-line valves	
Diaphragm valves	100
Bellows-sealed valves	100

[a] Although a control efficiency is not attained in all cases, it is achievable in some cases.

[b] This control effectiveness reflects the fact that a closed vent system is normally sized for emergency relief.

[c] This control efficiency reflects the use of these devices downstream of an initial valve with VOC on one side and atmosphere on the other.

Source: Goodwin, 1980

Compressors can sometimes be fitted with mechanical seals. Oil or compressed gas may be used depending on compatibility. Degassing vents and closed vent systems must be used in conjunction with mechanical seals. Closed vent systems can also be used to control emissions from compressor seal areas. Again, consideration must be given to preventing explosive conditions.

Rupture disks can be used to prevent VOC emissions from leaks due to faulty seating of pressure relief devices and safety valves. Corrosion or fatigue of the rupture disk itself may result in fugitive emissions.

Rupture disks may also be placed upstream of relief valves. In this application, block valves are placed upstream of the disks to facilitate disk replacement. Some means of testing the disk integrity is also necessary.

Closed vent systems can be used to control fugitive emissions from relief valves. If emergency flares are used to control these fugitive emissions, the destruction efficiencies might be much less than the 99+% for properly designed systems because of the very small flow rate from fugitive sources (Goodwin, 1980).

Caps, plugs, flanges or second valves can be used to control fugitive emissions from open-ended valves. Closed-loop sampling systems, instead of open-ended valves, eliminate emissions of purged fluids. Pressure differentials or safety requirements may prohibit the use of closed-loop samplers.

Diaphragm and bellows seal valves are not prone to fugitive emissions, however, they are not applicable to all process conditions.

3. Capture of Emissions and Rerouting to a Control Device

It is not practical to capture all fugitive emissions, especially when the leaks are from equipment seals. Fugitive emissions from sources such as pressure relief valves, in-line samplers, degassing tanks, water treatment works, and sewers can often be captured and sent to a control device. Many of the surveyed companies have already controlled fugitive emissions in this way. Seven of the 14 plants reported that at least some of their pressure relief devices were tied in to a flare, and some reduced their fugitive emissions estimate accordingly. Three plants reported that sampling lines were controlled: two were directed to a flare and the third was recovered by the process.

The reduction efficiency depends on the degree of capture and the design and other uses of the control device. If the fugitive emissions are directed to a continuously operating flare, perhaps designed to control emissions from process vents, the reduction efficiency would be very high. If an emergency flare is used as a control device, the large burner tips and other design features might not provide significant reductions.

C. Control of Emissions from the Storage of Chemicals

1. Fixed Roof Tanks

(a) Internal Floating Roofs

The purpose of a floating roof inside of a fixed roof tank is to eliminate the vapour space, hence, reduce emissions. Internal floating roofs can reduce emissions by about 90% (Burr et al, 1977) compared to fixed roof tanks. Emissions resulting from the evaporation of liquid clinging to walls or support columns, leaking through deck seams and through seals must be vented to prevent explosive conditions. Inert gas blankets can also be used.

Emissions from internal floating roof tanks may be further reduced by using liquid-mounted primary seals, continuous rim-mounted secondary seals, welded decks, gasketted fittings and flexible fabric seals to cover pipe columns.

Retrofitting existing fixed-roof tanks with internal floaters can often be paid out with the savings in "recovered" chemicals, especially when the vapour pressures of the chemicals are high. Not all fixed-roof tanks can be effectively retrofitted, however. Existing tanks may be out of round, they may have internal obstructions, they may require replumbing of support columns and they may require bracing or reinforcement.

Existing tanks must also be drained, vented and cleaned prior to retrofitting. Once in service, the internal floating roofs require periodic inspections for leaks and holes.

Typically, larger diameter fixed-roof tanks are more cost effective to retrofit than smaller tanks.

Many of the surveyed companies have already converted their fixed-roof tanks. A number of smaller fixed roof tanks still remain, however. Some manufacturers complained of freezing problems with the floating roofs when storing benzene. Insulation heat tracing and temperature monitoring systems were used to prevent freezing.

(b) Vapour Balancing Coupled with a Control Device

Emissions from storage tanks can be effectively controlled by capturing the vapours and passing them to a control device. Flares can be used, however, vent scrubbers are more common. Condensers can also be practical for controlling tank vent emissions. Six plants reported some form of vapour recovery on tank vents. Two used scrubbing systems, one flared recovered vapours and another recycled gases back into the process.

Below-ground storage tanks reduce emissions, especially in the summer, because of lower ground temperatures. Diurnal variations are also very minimal, so breathing losses are reduced.

The techniques for reducing storage VOC emissons are well developed and proven. They are widespread in the CCPA member companies. The potential for significant further reductions is very limited.

D. Control of Emissions from the Transfer of Chemicals

A good deal of the chemical transfers taking place at the surveyed companies is via pipeline to storage tanks for feed materials. Vapour balancing, per se, is then precluded. However, capture of fixed-roof storage tanks vent emissions during filling can be effectively controlled by capturing the emissions and routing them to a control device. The flow rate during filling via pipeline can be quite high, so the control system must be sized to handle the high rate, intermittent nature of the vents.

When transfer is between truck tank and fixed-roof storage tank, vapour balancing will reduce emissions temporarily, by 100%, less any fugitive losses in the balancing system. The destruction or recovery of the vapours from balancing operations must ultimately be achieved, either at the supply end, when the truck tanks carrying raw materials are filled, or at the manufacturing end when the product storage tanks are filled.

This technology is well developed and proven for gasoline marketing. A number of the surveyed companies are also using this technique. Five plants reported vapour recovery units on loading operations. Two directed loading losses to a flare, and two used scrubbing systems.

Reduction efficiencies are a function of the control device and the integrity of the balancing system. Fugitive emissions from balancing systems might typically run at 5%. Control efficiencies for recovery with carbon adsorption or refrigeration can run in excess of 90%. The degree of reduction is obviously great, however, because of the low contribution to total VOC emissions, implementation of this control technique would have minimal impact on overall emissions.

E. Socioeconomic Impacts

As mentioned earlier, the costs of controls and VOC reduction potentials are very site specific. Few generalizations can be drawn which are applicable to all chemical manufacturing industries. An attempt will be made to cover some of the common concerns voiced by the surveyed companies.

The nature of chemical manufacturing and the state of facilities makes the application of controls in a fairly applied manner very difficult. This is because there is no baseline level

of emissions which can be used as a yardstick for comparison purposes. It is obviously unfair to compare the emissions from a producer of one chemical product with those from a producer of a different chemical product. It is also unfair to compare emissions from plants which produce the same chemicals by different processes and possibly different feedstocks.

Companies which produce a variety of different products in a number of different units may have more of an opportunity for recirculating captured emissions or using closed-loop technology. One of the surveyed plants was able to collect its process emissions and use the VOCs in its gasoline manufacturing process next door.

Larger manufacturers or those producing multiple products may benefit from economies of scale or shared facilities with other units. Larger facilities often are more flexible with capital and manpower requirements.

Companies supplying the domestic market might have more of an opportunity to pass on additional costs to the consumer. Companies with heavy international competition will have to keep product prices in line with market rates.

Newer facilities typically tend to be tighter than older facilities. This is because it is usually more economical to design and build closed loops and recirculating schemes into new facilities than to retrofit existing facilities. Newer facilities then tend to emit less VOCs per tonne of product than older facilities. Newer facilities, however, may find it more difficult to reduce VOC emissions by a fixed percentage than older ones. Similarly, some of the manufacturing companies have recently invested to tighten up their facilities either for health, environmental or production efficiency reasons. These companies would also not be in as good a position in the future to reduce emissions by a fixed percentage.

For these and other reasons, the application of across-the-board regulations aimed at reducing emissions by a fixed percentage is inequitable. An alternative which may improve the fairness of VOC reduction regulations, would be to set limits on emissions per tonne of product. This at least allows for comparisons of like facilities -those using the same process and feedstocks to manufacture the same product. It may be, however, difficult for older, smaller plants to meet the same emission standards as those achievable for larger, newer plants.

A comprehensive analysis of the alternatives available for regulating VOC emissions is beyond the scope of this report.

V. IMPACTS OF CONTROLS FOR SURVEYED PLANTS

The control of VOC emissions from the chemical manufacturing industry has progressed at different rates between plants, according to the survey of CCPA representatives. There are a variety of reasons for these differences, such as, the age of the facility, the chemical(s) produced, the ease of control at an individual facility and the possibility of selling or using waste streams for producing other products. These differences in degree of VOC control from plant to plant make it impossible to estimate in detail the amount of reductions potentially achievable from the surveyed companies. A detailed estimation would have to be done on a plant by plant basis with considerable input from each of the surveyed companies.

An alternative to the detailed approach, is to lump individual companies together by chemical product and, based on discussions with representatives of the surveyed companies, assume reduction efficiencies and controllable fractions of the remaining uncontrolled emissions. This alternative should provide a good indication of the potential reductions achievable. When so much of an evaluation depends on the individual plant, an order of magnitude illustration is the best that can be achieved.

A spreadsheet of the process, storage, loading and fugitive emissions for each of the surveyed companies was produced. The spreadsheet itemized each of the sources reported in the questionnaires. Sources were marked as controlled or uncontrolled. This data was then used to produce summaries of controlled and uncontrolled emissions by chemical product type (Tables V-1 and V-2).

Discussions with representatives from most of the surveyed companies indicated a few sources which could not be readily controlled for safety or technical reasons. The uncontrolled VOCs were adjusted to produce an estimate of controllable VOC emissions. The controllable fraction amounted to 92% of the uncontrolled emissions. It should be noted that these controllable emissions are typically more costly and/or technically difficult to reduce than the emissions which have already been reduced. Typically, the high loss sources have already been recycled internally. The continuous process vents have already been directed to flares or boilers. Many fixed-roof tanks have been retrofitted with internal floaters. Consequently, many of the remaining sources are dilute streams or low VOC emitters.

A. Control Scenarios

1. Scenario 1 - Control of Process, Storage and Transfer Emissions

Total VOC emissions from the surveyed companies for 1988 as shown in Table III-1 are 10,143 tonnes. This includes 57 tonnes from spills. The remaining total is 10,086 tonnes. About 59% of these emissions, 5,940 tonnes, arise from process, storage and loading sources. Of this total, about 1,200 tonnes of VOCs are emitted from control devices. The remaining 4,740 tonnes of VOC are considered uncontrolled emissions. About 4,270 tonnes are estimated to be controllable based on discussions with the surveyed companies (meaning in this context those sources potentially

TABLE V-1 SUMMARY OF CONTROLLED AND UNCONTROLLED EMISSIONS BY SOURCE AND PRODUCT TYPE

Chemical	VOC Emissions in Tonnes		
	Controlled[a] Emissions	Uncontrolled[b] Emissions	Total Emissions
Process			
Styrene	125.4	157.0	282.4
BTX	21.8	17.5	39.3
EO/EG	198.9	614.5	813.5
Ethylene	513.1	1400.6	1913.6
Polyethylene	233.9	2062.6	2296.4
Maleic Anydride	0.0	77.1	77.1
Total Process	1093.1	4329.3	5422.4
Fugitive			
Styrene	120.0	134.6	254.6
BTX	60.0	150.8	210.8
EO/EG	0.0	160.9	160.9
Ethylene	700.0	1051.7	1751.7
Polyethylene	130.0	1631.3	1761.3
Maleic Anhydride	0.0	7.5	7.5
Total Fugitive	1010.0	3136.8	4146.8
Storage			
Styrene	1.2	188.6	189.8
BTX	51.0	75.0	126.0
EO/EG	0.5	0.3	0.8
Ethylene	14.9	10.6	25.5
Polyethylene	0.0	117.2	117.2
Maleic Anydride	0.0	4.6	4.6
Total Storage	67.6	396.3	463.9
Loading			
Styrene	0.0	5.8	5.8
BTX	8.9	6.7	15.6
EO/EG	0.1	0.2	0.3
Ethylene	28.2	0.0	28.2
Polyethylene	2.8	0.0	2.8
Maleic Anydride	0.0	0.0	0.0
Total Loading	40.0	12.7	52.7
TOTAL	2210.7	7875.1	10085.9

[a] Emissions from controlled sources
[b] Emissions from sources without controls

TABLE V-2 SUMMARY OF VOC EMISSIONS BY SOURCE TYPE AFTER SCENARIO 1 CONTROLS

VOC Emissions in Tonnes								
Chemical	Existing Controlled Emissions	Existing Uncontrolled Emissions	Existing Total Emissions	Breakdown of Existing Uncontrolled Emissions		Effect of Scenario 1		Total Emissions After Scenario 1
				Controllable	Uncontrollable	Reduction of Controllable Emissions	Remaining Emissions	
Process								
Styrene	125.4	157.0	282.4	105.0	52.0	75.6	29.4	206.8
BTX	21.8	17.5	39.3	17.5	0.0	12.6	4.9	26.7
EO/EG	198.9	614.5	813.5	380.7	233.8	274.1	106.6	539.3
Ethylene	513.1	1400.6	1913.6	1400.6	0.0	1008.4	392.2	905.3
Polyethylene	233.9	2062.6	2296.4	1883.2	179.4	1355.9	527.3	940.6
Maleic Anhydride	0.0	77.1	77.1	77.1	0.0	55.5	21.6	21.6
Total Process	1093.1	4329.3	5422.4	3864.1	465.2	2782.2	1081.9	2640.3
Fugitive								
Styrene	120.0	134.6	254.6				220.5	254.6
BTX	60.0	150.8	210.8				150.8	210.8
EO/EG	0.0	160.9	160.9				160.9	160.9
Ethylene	700.0	1051.7	1751.7				1051.7	1751.7
Polyethylene	130.0	1631.3	1761.3				1631.3	1761.3
Maleic Anhydride	0.0	7.5	7.5				7.5	7.5
Total Fugitive	1010.0	3136.8	4146.8	0.0	0.0	0.0	3136.8	4146.8
Storage								
Styrene	1.2	188.6	189.8	188.6		135.8	52.8	54.0
BTX	51.0	75.0	126.0	75.0		54.0	21.0	72.0
EO/EG	0.5	0.3	0.8	0.3		0.2	0.1	0.6
Ethylene	14.9	10.6	25.5	10.6		7.6	3.0	17.9
Polyethylene	0.0	117.2	117.2	117.2		84.4	32.8	32.8
Maleic Anhydride	0.0	4.6	4.6	4.6		3.3	1.3	1.3
Total Storage	67.6	396.3	463.9	396.3	0.0	285.3	111.0	178.6
Loading								
Styrene	0.0	5.8	5.8	5.8		4.2	1.6	1.6
BTX	8.9	6.7	15.6	6.7		4.8	1.9	10.8
EO/EG	0.1	0.2	0.3	0.2		0.1	0.1	0.2
Ethylene	28.2	0.0	28.2	0.0		0.0	0.0	28.2
Polyethylene	2.8	0.0	2.8	0.0		0.0	0.0	2.8
Maleic Anhydride	0.0	0.0	0.0	0.0		0.0	0.0	0.0
Total Loading	40.0	12.7	52.7	12.7	0.0	9.1	3.6	43.6
TOTAL	2210.7	7875.1	10085.9	4273.1	465.2	3076.6	4333.3	7009.3

amenable to further control). The breakdown for the emissions by source type is given in Table V-1.

Through discussions with some of the surveyed companies and review of the various sources which remain uncontrolled, the following assumptions were made:

- 80% of the controllable storage, loading and process emissions could be reduced through reasonably available control technologies (RACT);
- average in-use, combined capture/reduction efficiencies of 90% are achievable for control of storage, loading and process emissions. This takes into account capture losses, control device inefficiencies and control device down time.

The value of 90% is a reasonable estimate for illustrative purposes. Controls such as scrubbers on tank vents, were reported to reduce emissions by 65% in the survey. Flares could reduce emissions by 98% to 99+%. Condensers can reduce emissions by 50% to 90+% depending on operating conditions. Many control devices require periodic maintenance.

2. Scenario 2 - Control of All Emissions

Scenario 2 amounts to Scenario 1 plus control of fugitive emissions.

Fugitive emissions were estimated at about 4,147 tonnes from the surveyed companies. There was no consistent estimating methodology used to derive this figure, however. As shown in Table III-15, the method used to estimate fugitive emissions has a large impact on the derived value. Use of SOCMI factors result in estimates of fugitive emissions approximately 3 to 10 times what other methods indicate, based on a limited sampling. This is obvious from a review of the emission factors used in the various fugitive emission estimating methods given in Table II-1. Rough estimates indicate that if SOCMI factors were used consistently, fugitive emissions would be estimated at over 7,000 tonnes. If the more rigorous methods were used consistently, the fugitive emission estimate would be about one-half or around 2,000 tonnes. Until more work is done by industry to estimate fugitive emissions using the more rigorous methods, the value of 4,147 tonnes is still the best estimate at present.

A number of companies have reported control of their fugitive emissions by using non-leaking or low leaking parts, using double mechanical seals, collecting degassing vent emissions, sending relief valve emissions to control devices, etc. In many cases, the extent of fugitive emission controls is unclear.

Of the 10,090 tonnes from all sources, about 2,210 tonnes are controlled and 7,880 tonnes are uncontrolled. On the basis of the reported fugitive emissions of about 4,150 tonnes, using a variety of methods, approximately 1,010 tonnes are controlled and 3,140 tonnes are uncontrolled. The breakdown for fugitive emissions is shown in Table V-1. Control of these remaining uncontrolled emissions could result in about a

40% reduction. This is close to the minimum reduction efficiency attainable by leak detection and repair programs. The reduction from the use of low leak and non-leak equipment, closed-loop systems and capture of emissions and rerouting to a control device are assumed to be offset by uncontrollable fugitive emissions and inefficiencies in the fugitive emission control systems.

B. Potential VOC Emission Reductions

1. Reductions Under Scenario 1

The calculation of emissions after Scenario 1 is illustrated in Table V-2. Existing controlled emissions were assumed to remain at the inventoried level. Existing uncontrolled emissions were split into those potentially amenable to control (i.e. controllable) and those for various reasons uncontrollable. The controllable sources in this group were assumed controlled as described previously resulting in the values shown for emissions remaining after Scenario 1. Fugitive emissions were assumed to remain unchanged in Scenario 1. Potentially controllable emissions from process, storage and loading sources total about 4,270 tonnes. This could be reduced by 3080 tonnes. Emissions after Scenario 1 total 7,009 tonnes, a reduction of 30% from the current inventory.

The majority of the reduction in emissions resulting from Scenario 1 controls arises from reductions in process emissions. This results principally because emissions from storage and loading sources are comparatively small and the assumption in this case that no reductions are made in fugitive emissions.

Emissions are totalled by product type in Table V-3. This is a total of data from Table V-2.

2. Reductions Under Scenario 2

In Scenario 2, fugitive emissions are controlled to some extent and the controls achieved in Scenario 1 also apply. Table V-4 summarizes the details for calculation of emissions after Scenario 2 controls are implemented.

Scenario 2 leads to a further reduction in emissions of 1255 tonnes compared to Scenario 1. The reduction in fugitive emissions amounts to 30% of the pre-control amount. The reduction in fugitive emissions when combined with reductions in process, storage and loading emissions possibly by controls as described for Scenario 1 yield a total reduction of 4330 tonnes. This represents 43% of the existing emissions from all sources.

Emissions are totalled by product type in Table V-5.

TABLE V-3 EMISSIONS BY PRODUCT TYPE AFTER SCENARIO 1 CONTROLS

Chemical	VOC Emissions in Tonnes			
	Existing Total Emissions	VOC Removed by Additional Controls		Final Remaining Emissions
		(t)	(%)	
Styrene	732.6	215.6	29	517.0
BTX	391.7	71.4	18	320.3
EO/EG	975.5	274.4	28	701.1
Ethylene	3719.0	1016.0	27	2703.0
Polyethylene	4177.8	1440.3	34	2737.5
Maleic Anhydride	89.2	58.8	66	30.4
TOTAL	10085.9	3076.9	30	7009.3

TABLE V-4 SUMMARY OF VOC EMISSIONS BY SOURCE TYPE AFTER SCENARIO 2 CONTROLS

VOC Emissions in Tonnes								
Chemical	Existing Controlled Emissions	Existing Uncontrolled Emissions	Existing Total Emissions	Breakdown of Existing Uncontrolled Emissions		Effect of Scenario 2		Total Emissions After Scenario 2
				Controllable	Uncontrollable	Reduction of Controllable Emissions	Remaining Emissions	
Process								
Styrene	125.4	157.0	282.4	105.0	52.0	75.6	29.4	206.8
BTX	21.8	17.5	39.3	17.5	0.0	12.6	4.9	26.7
EO/EG	198.9	614.5	813.5	380.7	233.8	274.1	106.6	539.3
Ethylene	513.1	1400.6	1913.6	1400.6	0.0	1008.4	392.2	905.3
Polyethylene	233.9	2062.6	2296.4	1883.2	179.4	1355.9	527.3	940.6
Maleic Anhydride	0.0	77.1	77.1	77.1	0.0	55.5	21.6	21.6
Total Process	1093.1	4329.3	5422.4	3864.1	465.2	2782.2	1081.9	2640.3
Fugitive								
Styrene	120.0	134.6	254.6	134.6		53.8	80.8	200.8
BTX	60.0	150.8	210.8	150.8		60.3	90.5	150.5
EO/EG	0.0	160.9	160.9	160.9		64.4	96.5	96.5
Ethylene	700.0	1051.7	1751.7	1051.7		420.7	631.0	1331.0
Polyethylene	130.0	1631.3	1761.3	1631.3		652.5	978.8	1108.8
Maleic Anhydride	0.0	7.5	7.5	7.5		3.0	4.5	4.5
Total Fugitive	1010.0	3136.8	4146.8	3136.8		1254.7	1882.1	2892.1
Storage								
Styrene	1.2	188.6	189.8	188.6		135.8	52.8	54.0
BTX	51.0	75.0	126.0	75.0		54.0	21.0	72.0
EO/EG	0.5	0.3	0.8	0.3		0.2	0.1	0.6
Ethylene	14.9	10.6	25.5	10.6		7.6	3.0	17.9
Polyethylene	0.0	117.2	117.2	117.2		84.4	32.8	32.8
Maleic Anhydride	0.0	4.6	4.6	4.6		3.3	1.3	1.3
Total Storage	67.6	396.3	463.9	396.3	0.0	285.3	111.0	178.6
Loading								
Styrene	0.0	5.8	5.8	5.8		4.2	1.6	1.6
BTX	8.9	6.7	15.6	6.7		4.8	1.9	10.8
EO/EG	0.1	0.2	0.3	0.2		0.1	0.1	0.2
Ethylene	28.2	0.1	28.2	0.0		0.0	0.0	28.2
Polyethylene	2.8	0.0	2.8	0.0		0.0	0.0	2.8
Maleic Anhydride	0.0	0.0	0.0	0.0		0.0	0.0	0.0
Total Loading	40.0	12.7	52.7	12.7	0.0	9.1	3.6	43.6
TOTAL	2210.7	7875.1	10085.9	7409.9	465.2	4331.3	3078.6	5754.6

TABLE V-5 EMISSIONS BY PRODUCT TYPE AFTER SCENARIO 2 CONTROLS

Chemical	VOC Emissions in Tonnes			
	Existing Total Emissions	VOC Removed by Additional Controls		Final Remaining Emissions
		(t)	(%)	
Styrene	732.6	269.4	37	463.2
BTX	391.7	131.7	34	260.0
EO/EG	975.5	338.8	35	636.6
Ethylene	3719.0	1436.7	39	2282.4
Polyethylene	4177.8	2092.8	50	2085.0
Maleic Anhydride	89.2	61.8	69	27.4
TOTAL	10085.9	4331.3	43	5754.6

Fugitive emissions range between 2000 and 7000 tonnes, depending on the estimating methods used. Reductions achievable under Scenario 2 assumptions account for 30% of the total potential VOC reductions when using 4150 tonnes as the estimate of fugitive emissions. Therefore, it is reasonable to assume that reductions in fugitive emissions could account for between 15% and 50% depending on the estimating method used. Consequently, it is important to determine the contribution from fugitive emissions more accurately and consistently.

VI. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1. The estimate of VOC emissions in the 1988 inventory of 10,143 tonnes is substantially less than the estimate made in the preliminary 1985 inventory principally because many process emissions are controlled and because of improvements in methodology and source data.

2. VOC emissions from the surveyed chemical plants total 10,143 tonnes, with the majority originating from process and fugitive emission sources as shown below:

	VOC Emissions (t)	(%)
Process emissions	5422	53
Fugitive emissions	4147	41
Storage emissions	464	5
Loading	53	1
Total	10,130	100

Spills accounted for 57 tonnes.

3. Emissions of benzene, toluene, xylenes and styrene are shown in Table VI-1. BTX and styrene emissions account for 7.1% of the emission total.

4. The most widely used form of control of process emissions is flaring. Measurement data do not exist for the efficiency of these flares, however, the average value determined from supplier, engineering or literature sources was 96%.

5. Fugitive emissions were determined by the use of SOCMI factors, leak/no leak factors, stratified factors and stratified correlations. Based on data from plants which used more than one of these methodologies it is clear that: 1) fugitive emission estimates generally decrease as more detailed methodologies are used; and (2) the inventory total for fugitive emissions is likely an overestimate of actual emissions; and (3) use of SOCMI factors can lead to large overestimates in many cases.

TABLE VI-1 EMISSIONS OF BTX AND STYRENE

Chemical Produced	VOC Emissions (tonnes/year)					
	Total	Benzene	Toluene	Xylenes	Styrene	Other
BTX	393.1	91.9	82.4	76.3	--	141.6
EB/Styrene	738.5	186.1	16.6	--	64.2	471.6
EO/EG	976.0	--	--	--	--	976.0
Ethylene	3767.8	89.4	20.9	7.6	3.5	3645.7
Maleic Anhydride	89.2	63.4	--	25.9	--	0.0
Polyethylene	4178.3	--	--	--	--	4178.3
Total, All Plants	10142.9	430.8	119.9	109.8	67.7	9413.2
%		4.2	1.2	1.1	0.7	92.8

6. Because of small contributions made by storage and loading emissions to the total, little additional uncertainty in total VOC emissions would be introduced by use of simpler methodologies than those used in this study as long as they were developed appropriately.

7. The methodologies and data sheets used for process and fugitive emissions generally worked well. Plant-specific methodologies have to be used to arrive at estimates of VOC emissions from many sources. This background data was often not reported in sufficient detail for the estimate reported to be rigorously verified. Emission values were accepted as reported initially or after discussion with respondents.

8. There is a wide range of practises in use for minimizing fugitive emissions. Only about half of those surveyed documented what practises were in use. Fugitive emission reduction programs include specification of low-leakage equipment for some surveyed plants that were recently constructed and inspection and maintenance programs for some existing plants.

9. Further reductions to VOC emissions are technically possible for the surveyed plants, though plants generally reported that only the more difficult and costly to control sources remain. Control options for reduction of VOC emissions from the surveyed plants are very site specific.

10. A VOC reduction of 3077 tonnes, or 30% of the existing emissions, could potentially be achieved under Scenario 1 that was analyzed, which allows for control of currently "uncontrolled" process, storage and loading emissions.

11. A VOC reduction of 4331 tonnes, or 43% of the existing emissions, could potentially be achieved under Scenario 2 that was analyzed, which includes all surveyed emissions, except spills.

12. Many methods exist for reducing VOC emissions from the surveyed plants including add-on control devices, improvements to the process, and changes to operating and maintenance practises. These were reviewed, but meaningful estimates of costs could not be made because of their dependence on site-specific factors.

13. A considerable amount of information is available describing the various organic chemical manufacturing processes both from the surveyed companies and from literature sources. This provides insight into the nature of VOC emission sources in the chemical manufacturing industry. It was beyond the scope of this report to cover this area.

14. It is sometimes difficult to define what is a controlled VOC emission and what is uncontrolled because of the nature of the processes. It is not uncommon to use what might normally be considered "control devices", such as condensers, and activated carbon beds, as integral parts of the process. As such, these "control devices" are necessary parts of the process, which, if bypassed, would result in such high chemical losses that the process might be rendered uneconomical.

B. Recommendations

1. The survey of VOC emissions for the organic chemical industry should be expanded from the plants included in this study to cover substantially the whole of the industry in Canada with some cutoff in lower plant size.

2. The survey of the remaining organic chemical plants should be conducted with industry involvement, as in this study, simplified methodologies for storage and loading emissions, neglecting spills, and using the same methodologies as in this study for process and fugitive emissions. Respondents should be encouraged to use more detailed methods than SOCMI factors for fugitive emission estimation.

3. The survey of VOC emissions for the organic chemical industry should be expanded to include identification of individual VOC compounds at plants, rather than just total VOCs, BTX and styrene.

4. A study should be done to bring together available data from past EPA testing programs, suppliers and other sources and the destruction efficiency of flares for VOCs and specific chemicals under various operating and weather conditions. These results should be used to assess the reasonableness of the values used in this and other relevant VOC inventories.

5. A detailed long-term study should be conducted for selected plants to quantify the benefits and costs of inspection and maintenance programs implemented to reduce fugitive emissions. This would provide the data needed to assess the costs and benefits of various approaches to reduction of fugitive emissions for the organic chemical industry in general and identify the most successful approach.

6. In conjunction with a survey of all other organic chemical manufacturers, manuals of "state-of-the-art" practises for individual chemical sectors can be prepared. Several companies have already provided good process descriptions, some of which include their techniques for reducing VOC emissions. The U.S. EPA has already compiled data which will supplement the survey information.

VII. REFERENCES

API, 1983, "Evaporation Loss from Internal Floating Roof Tanks", American Petroleum Institute, Technical Bulletin 2519.

API, 1989, "Evaporative Loss from External Floating Roof Tanks", American Petroleum Institute Technical Bulletin 2517.

API, 1962, "Evaporation Loss from Fixed Roof Tanks", American Petroleum Institute, Technical Bulletin 2518.

Basdekis, H.S., Erikson, D.G., Parmele, C.S., and Standifer, R.L., 1980, "Organic Chemical Manufacturing - Volume 5 Adsorption, Condensation and Absorption Devices", EPA-450/3-80-027, PB81-220543, IT Enviroscience for U.S. EPA.

Berglund, R.L., Romano, R.R. and Randall, J.L., 1990, "Fugitive Emissions from the Ethylene Oxide Production Industry", Environmental Progress (Vol. 9, No. 1), February 1990, pp 10-17.

Berglund, R.L., 1990, "A Total Quality Control Approach to Fugitive Emissions Regulation and Control", a presentation to the U.S. EPA Negotiating Committee for Control of Fugitive Emissions of VOC from Equipment Leaks, January 16, 1990.

CMA, 1989, "Improving Air Quality: Guidance for Estimating Fugitive Emissions from Equipment", Chemical Manufacturers Association, Washington, D.C., January.

Edwards, W.C. and Wilkin, J.G., 1988, "VOC Emissions Inventory for the Organic Chemical Industry in Canada", Report by B.H. Levelton & Associates Ltd. for Environment Canada, September.

Edwards, W.C. and Levelton, B.H., 1987, "Vancouver Oxidant Study: Inventory of Volatile Organic Compound Emissions from Motor Fuel Marketing", Phase I, Report by B.H. Levelton & Associates Ltd. for Environment Canada, Contract KE 603-60-0768/01-SB.

EPA, 1985, "Compilation of Air Pollutant Emission Factors", Vol. I AP-42 4th Ed., U.S. EPA Office of Air Quality Planning and Standards.

Federal/Provincial Long Range Transport of Air Pollutants Steering Committee, 1990, "NO_x/VOC Work Group on Control Technologies.

Forrester, J.S. and LeBlanc, J.G., 1988, "A Cool Way to Reduce Emissions", Chemical Engineering, May 23, 1988, pp 145-150.

Geddes, R.S. and Kotyk, S., 1987, "Review and Assessment of Current Flaring Technology", SKM Consulting Ltd. for Environment Canada.

Goodwin, D.R., 1980, "VOC Fugitive Emissions in Synthetic Organic Chemicals Manufacturing Industry Background Information for Proposed Standards", EPA-450/3-80-033a, PB81-152167, U.S. EPA.

Hall, S.M., 1990, "Predicting the Performance of VOC Condensers", Air Waste Management Assoc., March 1990, pp. 404-407.

Kosusko, M. and Nunez, C.H., 1990, "Destruction of Volatile Organic Compounds Using Catalytic Oxidation", Air Waste Management Assoc., Feb. 1990, pp 254-259.

Levelton, B.H. et al, 1979, "Review of Surface Coating Industry Atmospheric Emission Sources and Control Technology", Report by B.H. Levelton & Associates Ltd., for Department of Fisheries and Environment, January.

Lovell et al, 1980, "Organic Chemical Manufacturing: Selected Processes", Volume 9, Report for U.S. EPA by IT Enviroscience, EPA 450/3-80-028d, PB81-220584.

Pohl, J.H. and Soelberg, N.R., 1985, "Evaluation of the Efficiency of Industrial Flares: Flare Head Design and Gas Composition", Energy and Environmental Research Corporation for U.S. EPA, EPA/600/2-85/106 - PB86-100559.

Pohl, J.H. and Soelberg, N.R., 1985, "Evaluation of the Efficiency of Industrial Flares: Flare Head Design and Gas Composition", Report for U.S. EPA by Energy and Environmental Research Corp., EPA/600/2-85/106, PB86-100559.

Radian, 1987, "Criteria Pollutant Emission Factors for the 1985 NAPAP (National Air Precipitation Assessment Program) Emissions Inventory", Report by Radian Corp. for the U.S. EPA, EPA/600/7-87/015, PB87-198735.

Radian, 1980, "Problem-Oriented Report: Frequency of Leak Occurrence for Fittings in Synthetic Organic Chemical Plant Process Units", Prepared for the U.S. EPA, Report EPA-600/2-81-003, September.

Radian, 1981, "Evaluation of Maintenance for Fugitive Emission Control", Prepared for the U.S. EPA, Report EPA-600/52-81-080, May.

Tessitore, J.L., Pinion, J.G. and Decresie, E., 1990, "Thermal Destruction of Organic Air Toxics", Pollution Engineering, March 1990, pp 58-68.

APPENDIX A

QUESTIONNAIRE PACKAGE FOR THE SURVEY: BACKGROUND AND INSTRUCTIONS; DATA SHEETS; AND EMISSION FACTORS AND EQUATIONS

CCPA/ENVIRONMENT CANADA SURVEY OF ATMOSPHERIC EMISSIONS OF VOLATILE ORGANIC COMPOUNDS IN 1988 FROM SELECTED ORGANIC CHEMICAL PLANTS:

BACKGROUND AND INSTRUCTIONS

1.0 BACKGROUND

Volatile organic compounds (VOC) are precursors of photochemical oxidants and can contribute under certain atmospheric conditions to the formation of ozone. Elevated ozone concentrations are recognized as a serious air pollution problem since they reduce lung function and cause damage to crops. The health problems associated with exposure to ozone are most acute in children and the aged.

Benzene, toluene, xylenes and styrene have been designated as priority substances under the Canadian Environmental Protection Act (Appendix I).

Under contract to Environment Canada, B.H. Levelton & Associates Ltd. prepared a preliminary inventory of VOC emissions from the organic chemical industry in Canada in 1988 using the best available data in the public domain. The results of this study were published in the report, "VOC Inventory for the Organic Chemical Industry" and circulated to the Canadian Chemical Producers Association for the information of its members. The current work involves preparation of an improved inventory of VOC emissions using plant specific process and equipment data.

A CCPA/Environment Canada working group has been formed to develop a detailed inventory of VOC emissions from major organic chemical plants in Canada. The instructions and data sheets contained in this document are to be used in the preparation of the inventory so that consistency of methodology and emission factors are maintained. The following instructions define the data to be assembled for the inventory, the agreed methodology to be used to calculate emissions and the form in which the data is to be compiled for return to B.H. Levelton & Associates Ltd.

2.0 GENERAL INSTRUCTIONS

The CCPA is cooperating in the preparation of an inventory of VOC and Benzene emissions from the following plants:

<u>Benzene/Xylenes/Toluene</u>

Esso, Sarnia, ON
Polysar, Sarnia/Corunna, ON
Shell, Sarnia, ON
Sunoco, Sarnia, ON
Carbochem, Hamilton, ON
Petro-Canada, Montreal, PQ

Ethylene

Alberta Gas Ethylene, Red Deer, AB
Esso, Sarnia, ON
Polysar, Sarnia, ON
Petromont, Varennes, PQ

Ethylene Oxide/Ethylene Glycol

Union Carbide, Prentis, AB
Union Carbide, Montreal, PQ
Dow Chemical, Fort Saskatchewan, AB

Polyethylene

CIL, Edmonton, AB
Dow Chemical, Fort Saskatchewan, AB
Novacor, Red Deer, AB
Dow Chemical, Sarnia, ON
Dupont, Sarnia, ON
Esso, Sarnia, ON
Novacor, Moore, ON

Malaeic Anhydride

Monsanto, La Salle, PQ

Styrene

Shell, Scotford, AB
Dow Chemical, Sarnia, ON
Polysar, Sarnia/Corunna, ON

The data sheets contained in this survey are to be completed by each of the plants in the above list.

Please follow the emission calculation methodologies described in this survey and complete the data sheets as indicated. Return the data sheets and other information requested herein to:

B.H. Levelton & Associates Ltd.
8805 Osler Street
Vancouver, B.C.
V6P 4G1

Attention: Mr. Wayne Edwards, P.Eng.

If there are any questions about the data that is to be provided, special circumstances that make the suggested calculation

methodologies inappropriate for some emission sources, reporting of the results, or other issues, contact:

Mr. Helmut Burke, P.Eng., or

Mr. Wayne Edwards, P.Eng.

at (604) 266-1411 Telephone
(604) 266-0130 Facsimile

A glossary of terms is included in this document so all respondents have the same interpretation of the terminology used.

3.0 EMISSION SOURCES INCLUDED IN THE INVENTORY

The VOC emission inventory includes the following types of sources:

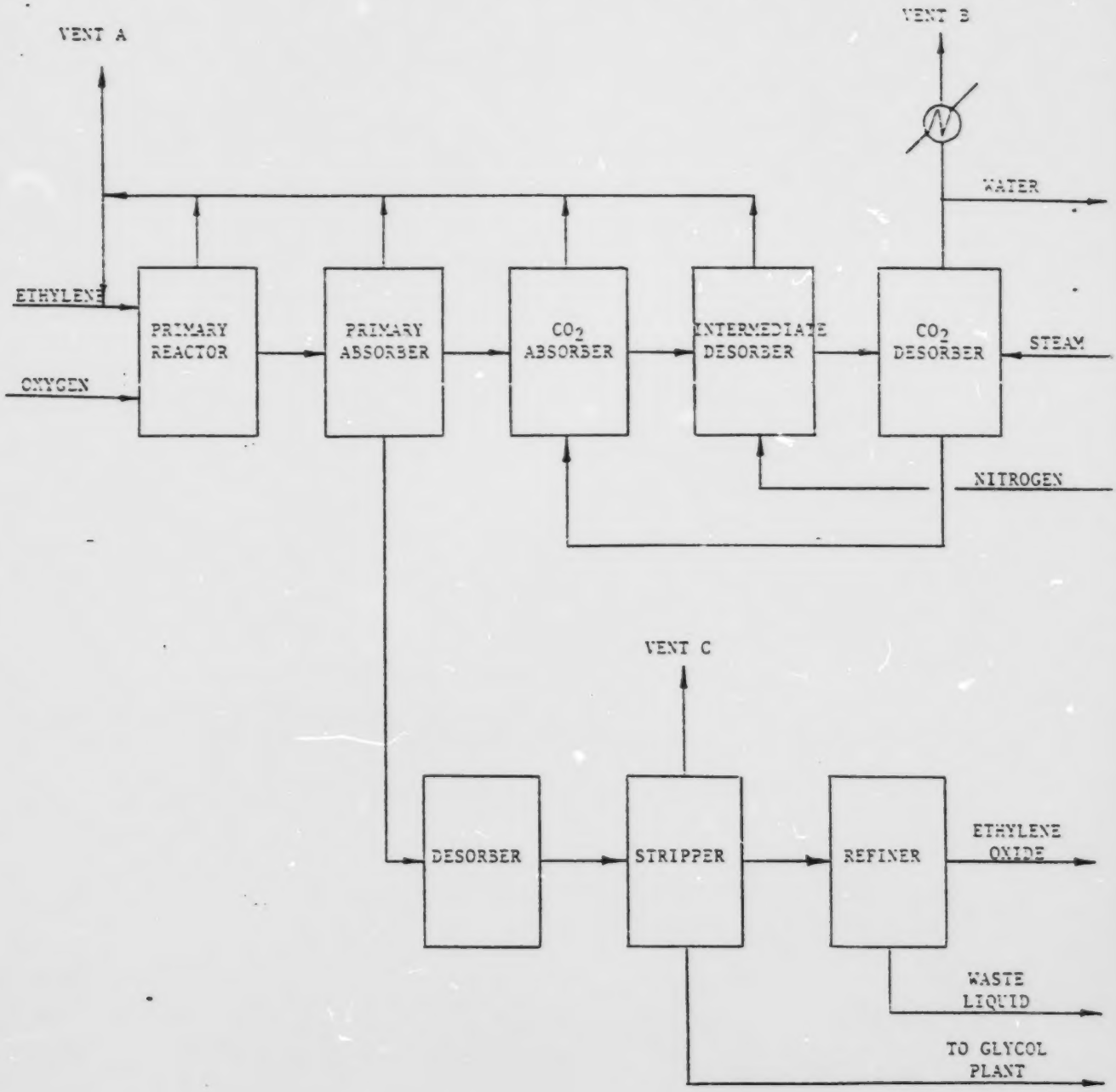
- process sources such as continuous vents and flares;
- fugitive leaks from process equipment such as pump seals, flanges, etc.;
- storage tanks and transfer of chemicals for shipment;
- spills/accidental discharges to atmosphere.

Methodologies and accepted factors or empirical relationships will be used for sources present in the plants. This document is organized by the above four general source categories. <u>All emissions are to be calculated for the 1988 calendar year</u>.

4.0 PROCESS EMISSIONS

1. Simplified Process Block Diagram

Provide a simplified block-type process flow diagram for the production plant included in the inventory. The diagram should show and label major unit processes in the plant, main flow stream, vents to atmosphere, vents to control equipment, waste residue streams, sumps that may emit VOCs, relief valves and rupture disks and any other points of discharge of VOCs to the atmosphere. Attached is a sample flow diagram.



EXAMPLE PROCESS BLOCK DIAGRAM BASED ON ETHYLENE OXIDE

2. VOC Control Equipment

Provide information about the VOC control equipment, including flares, used on any process sources. This information will be used in conjunction with available calculation methodologies for uncontrolled source emissions to determine actual VOC emissions to the atmosphere. A thorough description of the type and performance of the control equipment is needed to ensure that VOC emissions can be calculated accurately.

Fill in Table 1 for each control system used for process sources. Use a separate copy of Table 1 for each control system and use additional separate sheets if more space is required. Use the same identification system for the control system as shown in the process diagram.

3. Emission Calculations for Process Sources

Emissions from process sources are to be calculated using base quantities, emission factors and control efficiencies according to the following equation:

$$E_i = BQ_i \times EF_i \times \frac{(100 - CE_i)}{100}$$

where

E_i - annual VOC emission for source i, kg
BQ_i - base quantity for source i, tonnes or m^3
EF_i - emission factor for source i, kg/t or kg/m^3
CE_i - VOC removal efficiency of control equipment, %

Emissions should be calculated for each of the sources listed for the plant production unit in Appendix II. It is possible that your plant has sources for which no emission factors exist, has sources that are similar but have higher or lower emission characteristics, or is designed in such a way that the sources present are not the same as those listed for the process in Appendix II. Consequently, take care when selecting emission factors and include comments for those sources which do not fit the standard source classifications.

Use Table 2 to summarize and report emissions from process sources derived using emission factors and base quantities. The control efficiencies used in Table 2 should be annual average values, allowing for upsets, downtime and other factors that affect the normal performance of the

control system. Give the weight percent of benzene, toluene, xylene, and styrene present in the emitted VOCs, where data are available.

For sources included in Table 2 above, as well as those that cannot be analyzed using emission factors, estimate emissions using best available data for hours of discharge, flow rate, VOC concentration and level of control. Use Table 3 to record the basis and final results of these calculations. Show assumptions used for the analysis, sources of data and units for data. Included in process emissions are those that originate from flares. Insure that these emissions are included in Tables 1 and 2, where applicable.

Give the heights of all process emissions from stacks and flares that are at a height of 30 m or more.

4. Emission Calculations for Intermittent Sources

VOC emissions sometimes occur when cleaning or venting process vessels and when starting up or shutting down a production unit. These are not included in the estimates of emissions calculated using emission factors (Section 3). Intermittent sources are to be quantified in the summary sheet given in Table 4. Please give a brief description of the source, typical annual hours of discharge, estimated VOC concentration of discharge and the annual emission estimate. Record the units of the quantities if they differ from the ones shown.

5.0 FUGITIVE EMISSIONS

Fugitive emissions are to be calculated for:

Source	Service
Valves	Gas Light liquid Heavy liquid
Pump Seals	Light liquid Heavy liquid
Compressor Seals	Gas/Vapour
Pressure Relief Seals	Gas/Vapour

Source	Service
Flanges	
Open-Ended Lines	
Sampling Connections	

Emissions should be calculated for these source categories and reported for each major unit process identified in the simplified process block diagram (4.1), and total plant.

Use the summary data sheet given in Table 5A for each major unit process identified in your process block diagram and for the total plant. Ensure that the plant area is stated in each case. Individual data sheets are provided (Tables 5B to 5G) for each fugitive emission source in each unit process area of the plant. These detailed data sheets (Tables 5B to 5G) allow for entry of source data needed for the CMA survey, but only the data marked with a "*" is essential for preparation of the inventory update. The detailed data sheets should be kept as backup.

The VOC composition data provided in Table 5A should represent the average for the identified unit process. This may be approximated, if better data is not available, as the average of the compositions of all inlet and outlet streams.

Included in Appendix III are emission factors for use of the leak/no-leak calculation methodology. The average SOCMI factors given in Table 5A are to be used for all emission estimates reported for this inventory. One of the more refined methods that are available for calculation of fugitive emissions, such as leak/no leak, may be used at some future date.

A description of operating and maintenance practices at the plant, such as leak detection and repair methods and specification of process equipment which is designed, used to minimize or prevent leaks should accompany Table 5A for the total plant. Use a separate sheet for this description.

6.0 STORAGE AND LOADING EMISSIONS

1. Storage Tanks for Feed, Intermediates and Products

Emissions from above-ground tanks are to be calculated using API/US EPA equations given in Appendix IV. Use Table 6 to enter tank data and emissions for fixed roof tanks. Use Tables 7 and 8 to enter tank data and emissions from external

and internal floating roof tanks respectively. State the chemical st. ed in the tank and VOC speciation data.

If VOC control equipment is used to reduce tank emissions, fill in Table 1 for each system used and note on Tables 6, 7 and 8 which tanks are connected to these controls so that the actual emission to atmosphere can be calculated. Use a separate sheet if more space is needed for your response.

2. Loading Operations

VOC emissions may occur from loading of your plant's products into tank cars, trucks or other shipment containers. If these operations occur at the plant, summarize the emission calculations in Table 9. Calculate emission factors appropriate to the mode of shipment and method of loading using equations given in Appendix V. Although emission factors for loading marine vessels are not available, give all other data in Table 9 for these emissions.

7.0 SPILLS/ACCIDENTAL DISCHARGES TO ATMOSPHERE

In Table 10, list and quantify discharges from relief valves, rupture disks and liquid spills from the plant for the last 3 years which resulted in emissions of VOCs. Give average annual VOC emission at the end of the table.

GLOSSARY

Combustion efficiency - the degree to which all fuel materials have been completely oxidized.

Compressor - device used to compress process gas and driven by rotary or reciprocating shafts.

Control efficiency - a measure of the performance of a control system in recovering or combusting compounds expressed as the ratio of the weight of VOC removed to the weight of VOC input, times 100.

Control system - systems of piping, instrumentation and equipment designed to recover or combust volatile organic compound emissions.

Control technique - leak detection and repair methods applied to reduce fugitive emissions and specification of process equipment which is designed to prevent leaks.

Destruction efficiency - a measure of the degree of destruction of a particular fuel material.

Emission factor - the per component mass emission rate applicable to populations of sources, not individual component measurements.

Flanges - bolted, gasket-sealed junctions.

Fugitive emissions - equipment leaks in chemical processing units.

Heavy liquid - a fluid with vapour pressure less than 0.3 kPa at 20°C.

Leak definition - monitoring instrument reading selected as the trigger value for initiating some action such as maintenance; e.g., 10,000 ppmv is the leak definition used by EPA.

Leaking emission factor - the per component mass emission rate associated with the population of sources with screening concentrations at or above the leak definition.

Leaking source - a source whose screening concentration is greater than or equal to 10,000 ppmv.

Light liquid - a fluid with vapour pressure greater than 0.3 kPa at 20°C.

Mass emissions rate - the quantity of volatile organic compound(s) released to the atmosphere in terms of total mass per unit time.

Non-leaking emission factor - the per component mass emission rate associated with the population of sources with screening concentrations less than the leak definition.

Open-ended lines - valves installed in a system so that they function with the downstream line open to the atmosphere.

Priority substance - a substance that has been given priority for assessment whether it is toxic or capable of becoming toxic as required by the Canadian Environmental Protection Act, Subsection 12 (1).

Process emissions - emissions that result from the venting of inlet gases, the release of volatiles that cannot be economically captured, and upset releases.

Pump - device used for movement of organic liquids.

Safety relief valves - spring-loaded valve designed to open when the process pressure exceeds a set pressure.

Sample connections - a place where representative samples are withdrawn from the process and where liquid or vapour purged from the sample line is drained onto the ground or into a sewer drain.

Seal - device isolating the process fluid from the atmosphere.

Secondary emissions - evaporation of VOC from solid, liquid and aqueous wastes generated within the process.

Source - a location within the plant boundary whose organic compounds may be released to the atmosphere or to a control system.

Spill - unplanned and not recovered release of volatile organic compounds or priority substances that have been reported to provincial or local authorities.

Uncontrolled emissions - emissions that would be emitted to the atmosphere in the absence of any add-on control device, but after any material recovery devices that constitute part of the normal material recovery operations in a process line where potential emissions are recoverable for recycle or resale.

Unsafe-to-monitor equipment - equipment that exposes monitoring personnel to an immediate danger while screening the equipment.

Valve - a device with a stem and seal that is in contact with the process fluid, gas or vapour.

Volatile organic compound (VOC) - non-methane hydrocarbon.

CCPA/ENVIRONMENT CANADA SURVEY OF ATMOSPHERIC EMISSIONS OF VOLATILE ORGANIC COMPOUNDS IN 1988 FROM SELECTED ORGANIC CHEMICAL PLANTS: EMISSION FACTORS AND EQUATIONS

APPENDIX I

ENVIRONMENT CANADA

PRIORITY SUBSTANCES LIST

PRIORITY SUBSTANCES LIST WITH CHEMICAL ABSTRACTS REGISTRY NUMBER

Group 1
- Arsenic (7440-38-2) and its compounds
- Benzene (71-43-2)
- Effluents from pulp mills using bleaching
- Hexachlorobenzene (118-74-1)
- Methyl tertiary-butyl ether (1634-04-4)
- Polychlorinated dibenzodioxins
- Polychlorinated dibenzofurans
- Polycyclic aromatic hydrocarbons
- Waste crankcase oils

Group 2
- Cadmium (7440-43-9) and its compounds
- Chlorinated waste water effluents
- Chlorobenzene (108-90-7)
- Chromium (7440-47-3) and its compounds
- Creosote-impregnated waste materials
- Dibutyl phthalate (84-74-2)
- 1,2-Dichlorobenzene (95-50-1)
- 1,4-Dichlorobenzene (106-46-7)
- 1,2-Dichloroethane (107-06-2)
- Dichloromethane (75-09-2)
- Di-n-octyl phthalate (117-84-0)
- bis(2-Ethylhexyl) phthalate (117-81-7)
- Inorganic fluorides
- Nickel (7440-02-0) and its compounds
- Pentachlorobenzene (608-93-5)
- Styrene (100-42-5)
- Tetrachlorobenzenes
- 1,1,2,2-Tetrachloroethane (79-34-5)
- Tetrachloroethylene (127-18-4)
- Toluene (108-88-3)
- Trichlorobenzenes
- 1,1,1-Trichloroethane (71-55-6)
- Trichloroethylene (79-01-6)
- Xylenes (1330-20-7)

Group 3
- Aniline (62-53-3)
- Benzidine (92-87-5)
- Chlorinated paraffin waxes (63449-39-8)
- bis(2-Chloroethyl) ether (111-44-4)
- bis(chloromethyl) ether (542-88-1)
- Chloromethyl methyl ether (107-30-2)
- 3,3-Dichlorobenzidine (91-94-1)
- 3,5-Dimethylaniline (108-69-0)
- Methyl methacrylate (80-62-6)
- Mineral fibres
- Organotin compounds (non-pesticidal uses)

APPENDIX II

PROCESS EMISSION FACTORS

SCC	PROCESS	UNCONTROLLED EMISSION FACTOR				BASE QUANTITY
		VOC	REF	BENZENE	REF	
Ethylene Oxide						
301174-01	General	3.9	01			t produced
-02	Air-oxidation process Reactor-Main vent	1.4	01			t produced
-10	Oxygen-oxidation Process Reactor - CO_2 purge vent	4.0	01			t produced
-11	Oxygen-oxidation process Reactor-Argon purge vent	10.9	01			t produced
-21	Stripper purge vent	0.002	01			t produced
-80	Fugitive emissions - general	76,200	01			process-unit year
Ethylene Glycol						
301251-01	General					t produced
-02	Evaporator purge vent	0.475	01			t produced
-03	Water removal stream - jet ejector	0.6	01			t produced
-04	Distillation column vent	0	01			t produced
-80	Fugitive emissioins - general	10,886	01			process unit year
Ethylene - General Process						
301197-01	General	0	01			t produced
-41	Flue gas vent	0.43	01			t produced
-42	Pyrolysis furnace decoking	0	01			t produced
-43	Acid gas removal	0.01	01			t produced
-44	Catalyst regeneration	0	01			t produced
-45	Compressor lube oil vent	7.3	01			t produced
-49	Fugitive emissions - general	315,250	01			process unit year

SCC	PROCESS	UNCONTROLLED EMISSION FACTOR				BASE QUANTITY
		VOC	REF	BENZENE	REF	
Ethylene - from Naphtha Gas/Oil						
301197-	Intermittent emissions					
	- single compressor train			0.791	02	t produced
	- dual compressor train			0.101	02	t produced
	Storage tanks			0.147	02	t produced
	Charge gas compressor lube oil vent					
	- single compressor train			0.0002	02	t produced
	- dual compressor train			0.0004	02	t produced
	Fugitive emissions - uncontrolled			0.0459	02	t produced
	Secondary waste water			0.0217	02	t produced
Ethylbenzene						
301169-01	General	.005	01			t produced
-02	Alkylation reactor vent	0	01			t produced
-03	Benzene drying	0	01			t produced
-04	Benzene recovery/recycle	0	01			t produced
-05	Ethylbenzene recovery	0	01			t produced
-06	Polyethylbenzene recovery	0	01			t produced
-80	Fugitive emissions - general	149,230	01			process unit year
301169-*	Atmospheric/pressure Column vents	2.6	04	1.2	02	t styrene produced
	Secondary emissions (waste water)	0.088	0.4	0.067	02	t styrene produced
	Benzene/toluene vacuum vent			3.0	02	t styrene produced
	Other vacuum vents			0.05	02	t styrene produced
	Hydrogen separation tank			0.003	02	t styrene produced
	Storage and handling	0.67	04	0.57	02	t styrene produced
	Alkylation reactor area vents	0.88	04	0.3	02	t styrene produced
	Fugitive emissions	0.51	04	0.11	02	t styrene produced
	Emergency vent on H_2 separator	0.008	0.4			

* All emission factors are based on analysis of a model 300,000 t/yr plant producing styrene from benzene and ethylene feed. Emission factors apply to an integrated plant and are averages and estimates derived from actual plant data. Vents apply to multiple sources. SCC categories not assigned.

SCC	PROCESS	UNCONTROLLED EMISSION FACTOR				BASE QUANTITY
		VOC	REF	BENZENE	REF	
Styrene						
301206-01	General	16.5	01			t produced
-02	Benzene recycle	0.3	01			t produced
-03	Styrene purification	6.0	01			t produced
-80	Fugitive emissions - general	112,490	01			process unit year
Polyethylene (high density)						
301018-07	General	18	01			t produced
-08	Monomer and solvent recovery	12.7	01			t produced
-09	Extruder	5.5	01			t produced
-10	Conveying - closed loop drying system	0.23	01			t produced
-11	Polymer fluff storage and mixers	0.005	01			t produced
Polyethylene (low density)						
301018-12	General	3.85	01			t produced
-13	Recovery and purification system	30.0	01			t produced
-14	Extruder	30.0	01			t produced
-15	Pellet silo	0	01			t produced
-16	Transfer/handling/ loading/packing	0	01			t produced
Polyethylene - All Types						
301018-60	Recovery system	20	01			t produced
-61	Purification system	15	01			t produced
-63	Extruder	15	01			t produced
-64	Pellet silo/storage	0	01			t produced
-65	Transfer/conveying	0	01			t produced
-66	Packing/shipping	0	01			t produced

SCC	PROCESS	UNCONTROLLED EMISSION FACTOR				BASE QUANTITY
		VOC	REF	BENZENE	REF	
Benzene Production						
301258-01	General	0	01			t produced
-02	Reactor	0.15	01			t produced
-03	Distillation vent	0.40	01			t produced
Toluene Production						
301258-05	General	0	01			t produced
-06	Reactor	0.15	01			t produced
-07	Distillation vent	0.40	01			t produced
Mixed Xylenes						
301258-15	General	0	01			
-16	Reactor	0.15	01			
-17	Distillation vent	0.40	01			
Aromatics - Fugitive						
301258-80	Fugitive - general	171,900	01			process unit year
Maleic Anhydride (from benzene)						
301100-02	Product recovery absorber	87.0	01	67	03	t produced
-03	Vacuum system vent	0.1	01			t produced
-04	Briquetting	0	01			t produced
-05	Secondary Sources - dehydration column, vacuum system, fractionation system	0.1	01			t produced
	Storage and handling	1.27	03	1.23	03	t produced
	Fugitive	1.24	03	1.13	03	t produced

REFERENCE KEY

01 Radian Corporation, 1987, "Criteria Pollutant Emission Factors for the 1985 NAPAP Emission Inventory", U.S. EPA, Con/tract 68-02-3994, No. 83.

02 U.S. EPA, 1988, "Toxic Air Pollutant Emission Factors - A Compilation for Selected Air Toxic Compounds and Sources", EPA-450/2-88-006a, October.

03 U.S. EPA, 1980, "Organic Chemical Manufacturing", Volume 6, EPA 450/3-80-028a, p. 208 and 213, Dec.

04 U.S. EPA, 1980, "Organic Chemical Manufacturing", Volume 6, EPA 450/3-80-028a, p. 290, Dec.

APPENDIX III

EMISSION FACTORS FOR FUGITIVE SOURCES

TABLE III-1 AVERAGE SOCMI EMISSION FACTORS FOR FUGITIVE EMISSIONS

	EQUIPMENT	SERVICE	EMISSION FACTOR (kg/hr/source)
1.	Valves	Gas	0.0056
		Light Liquid	0.0071
		Heavy Liquid	0.00023
2.	Pump Seals	Light Liquid	0.0494
		Heavy Liquid	0.0214
3.	Compressor Seals	Gas/Vapour	0.228
4.	Pressure Relief Seals	Gas/Vapour	0.104
5.	Flanges	All	0.00083
6.	Open-Ended Lines	All	0.0017
7.	Sampling Connections	All	0.0150

TABLE III-2 ALTERNATE LEAKING AND NON-LEAKING EMISSION FACTORS FOR FUGITIVE EMISSIONS (kg/hr source)

EQUIPMENT	SERVICE	LEAKING (≥ 10,000 ppm) EMISSION FACTOR (kg/hr/source)	NON-LEAKING (< 10,000 ppm) EMISSION FACTOR (kg/hr/source)
1. Valves	Gas[a]	0.0451	0.00048
	LL[b]	0.0852	0.00171
	HL[c]	0.00023[d]	0.00023
2. Pump Seals	LL	0.437	0.0120
	HL	0.3885	0.0135
3. Compressor Seals[e]	Gas	1.608	0.0894
4. Pressure Relief Valves	Gas	1.691	0.0447
5. Flanges	All	0.0375	0.00006
6. Open-Ended Lines	All	0.01195	0.00150

[a] The leaking and non-leaking emission factors for valves in gas/vapour service are based upon the emission factors determined for gas valves in ethylene, cumene, and vinyl acetate units during the SOCMI Maintenance Study.

[b] LL - light liquid service.

[c] HL - heavy liquid service.

[d] Leaking emission factor assumed equal to non-leaking emission factor since the computer leaking emission factor (0.00005 kg/hr/ source) was less than non-leaking emission factor.

[e] Emission factor reflects existing control level of 60 percent found in the industry; control is through the use of barrier fluid/ degassing reservoir/vent-to-flare or other seal leakage capture system.

APPENDIX IV

EQUATIONS FOR CALCULATION OF VOC EMISSIONS FROM ABOVE-GROUND TANKS

EPA FORMULAS FOR CALCULATING EMISSIONS FROM ABOVE-GROUND STORAGE TANKS

A. Fixed Roof Tanks

Vapour emissions from vented fixed roof tanks which do not have emission control equipment installed, occur from natural breathing of the tank with fluctuations in ambient temperature and pressure, and from the rise and fall of the liquid level in the tank during use.

The following equations apply to tanks with vertical cylindrical shells and fixed roofs, excluding insulated tanks, that store organic liquids at approximately atmospheric pressure. The total VOC emission (L_T) can be calculated as:

$$L_{TOTAL} = L_s + L_w$$

where L_s - fixed roof standing loss
L_w - fixed roof working loss

1. Breathing Loss

The relationship for breathing or standing loss is:

$$L_s = 8.712 \times 0.0226\ M_v\ (P/(P_{amb} - P))^{0.68}\ D^{1.73}\ H_v^{0.51}\ \Delta T^{0.5}\ F_p\ C_d\ K_c$$

where

L_s - standing loss from the tank (kg/yr)
M_v - molecular weight of the vapour in the tank (g/mol)
P - true vapour pressure at temperature (kPa)
P_{amb} - ambient pressure (kPa)
D - tank diameter (m)
H_v - average vapour space height in the tank, including cone roof height correction. To correct for a cone roof, include a vapour-space height equal to one-third of the height of the cone.
ΔT - average diurnal variation in temperature (°C)
F_p - a factor to account for the effect of tank colour
C_d - a factor to account for the effect of tank diameter
K_c - a factor to adjust for crude oil storage
- 1 for organic chemicals

Tank Colour - F_p

Roof	Shell	Paint Factor, F_p Good Condition	Poor Condition
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminum (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44
Medium gray	Medium gray	1.40	1.58

Diameter Adjustment for Small Tanks - C_d

For diameter $\geq$ 9.1 m, C = 1

For diameter < 9.1 m, $C = 0.2530\ D - 0.0140\ D^2 - 0.1334$

with D, the diameter of the tank, expressed in meters.

Liquid Temperature

The chemical property parameters used in the equation must be determined at its average bulk temperature over the year. This may be different to the ambient temperature depending on the temperature of incoming material and tank colour.

The average storage temperature for unheated and uninsulated tanks is:

Tank Colour	Liquid Temperature (°C)
White	$T_{amb} + 0$
Aluminum	$T_{amb} + 1.4$
Gray	$T_{amb} + 1.9$
Black	$T_{amb} + 2.8$

The U.S. EPA recommends that the vapour space height be assumed equal to 50% of the tank height when specific data is not available.

Molecular weights and true vapour pressures of selected petroleum liquids and volatile organic liquids are given in the table at the end of this Appendix.

2. Working Loss

The metric equation for working losses from fixed roof tanks is:

$$L_w = 1.738 \times 10^{-2} \times 0.024\ M_v\ P\ K_t\ K_c\ Q$$

where

L_w - working loss from the tank (kg/yr)
M_v - molecular weight of the vapour at temperature (g/mol)
P - true vapour pressure at temperature (kPa)
K_t - a factor to account for the effect of the number of tank turnovers
- $\frac{180 + N}{6N}$ for greater than 36 turnovers per year
- 1 for 36 turnovers per year or less
K_c - a factor to adjust for crude oil storage
- 1 for organic chemicals
Q - annual throughput (m^3)
N - annual throughput/tank capacity, dimensionless

B. External Floating Roof Tanks

Losses occur from floating roof tanks by leakage of vapour past the rim seal on the floating roof, by evaporation of the fuel film left on the wall as the liquid level drops and by leakage from roof fittings. Relationships have been developed by the API for these types of losses for liquids that are not boiling, have a true vapour pressure of 10 kPa to 101 kPa, average wind speed of 3 km/h to 24 km/h and a tank diameter of 6 m or greater, as given below.

Emissions from external floating roof tanks are the total of the rim seal loss, the withdrawal loss and the roof fitting loss.

1. Seal Loss

The metric relationship for seal losses is:

$$L_s = 1.488\ K_s\ (0.621V)^n\ P^*\ D\ M_v\ K_c$$

where

L_s - seal loss from the tank (kg/yr)
K_s - a factor to account for the effect of the seal design
V - average wind speed (km/h)
n - a factor to account for the effect of seal design
P^* - $\dfrac{P/P_{amb}}{(1 + (1 - P/P_{amb})^{0.5})^2}$
P - vapour pressure at temperature (kPa)
P_{amb} - ambient pressure (kPa)
D - tank diameter (m)
M_v - vapour molecular weight (g/mol)
K_c - a factor to adjust for crude oil storage
- 1 for organic chemicals

K_s and n for various seal types for external floating roof tanks and average fitting seals:

SEAL	WELDED TANKS		RIVETED TANKS	
	K_s	n	K_s	n
Mechanical shoe seal				
Primary seal only	1.2	1.5	1.3	1.5
With shoe mounted secondary seal	0.8	1.2	1.4	1.2
With rim mounted secondary seal	0.2	1.0	0.2	1.6
Liquid mounted resilient seal				
Primary seal only	1.1	1.0	NA	NA
With weather shield	0.8	0.9	NA	NA
With rim mounted secondary seal	0.7	0.4	NA	NA
Vapour mounted resilient seal				
Primary seal only	1.2	2.3	NA	NA
With weather shield	0.9	2.2	NA	NA
With rim mounted secondary seal	0.2	2.6	NA	NA

The colour of the tank affects the liquid temperature. For unheated white tanks, the liquid temperature can be taken to be ambient temperature. See Section A1 for tanks of other colours.

Average annual wind speed, V, for some Canadian cities are:

Edmonton	13.4 km/h
Red Deer	15.7 km/h
Sarnia	17.7 km/h
Hamilton	17.7 km/h
Montreal	11.7 km/h

Molecular weights and true vapour pressures of selected petroleum liquids and volatile organic liquids are given in the table at the end of this Appendix.

2. Withdrawal Loss

The losses from evaporation of liquid left on the wall of the tank as the roof level drops may be estimated using the equation:

$$L_w = 0.004 \frac{C\ W_l\ Q}{D}$$

where

L_w - withdrawal loss from the tank (kg/yr)
C - clingage factor which accounts for the amount of liquid left on the wall ($m^3/1000\ m^2$)
W_l - density of the liquid (kg/m^3)
D - tank diameter (m)
Q - annual working throughput (m^3). This is the throughput which results in raising and lowering of the floating roof.

There is no data available for the clingage factor to be used for organic chemicals. The best available data applies to gasoline and crude oil, which is given below. Use judgment when selecting a factor appropriate to your tank calculation.

CLINGAGE FACTOR, C ($m^3/1000\ m^2$)

PRODUCT	SHELL CONDITION		
	LIGHT RUST	DENSE RUST	GUNITE-LINED
Gasoline	0.002567	0.01283	0.2566
Single component stocks	0.002567	0.01283	0.2566
Crude oil	0.0103	0.0513	1.0266

3. Roof Fitting Loss

Roof fitting losses (L_{RF}) from external floating roof tanks can be estimated by the following equation:

$$L_{RF} = 0.4536\ F_F\ P^*\ M_v\ K_c$$

where

L_{RF} - roof fitting loss from the tank (kg/yr)
F_F - total roof fitting loss factor from Figure IV-1 and Figure IV-2 in original units (lb-mol/yr)
P^* - $\dfrac{P/P_{amb}}{(1 + (1 - P/P_{amb})^{0.5})^2}$
M_v - vapour molecular weight (g/mol)
K_c - a factor to adjust for crude oil storage
- 1 for organic chemicals

The following figures for average roof fitting loss factors were taken from the report "Evaporative Loss from External Floating-Roof Tanks" (API, 1989). The graphs have been left in the imperical units orginally used to avoid error from unit conversions. The roof fitting factor taken from the graphs should be used in the loss equation without changing units, since the conversions from pounds to kilograms is done in the loss equation.

Roof fitting loss factors have been developed for particular roof fittings. Graphs of these factors are given in API publication 2517 (1989), along with a description of the method for calculating the total roof fitting loss factor

from specific information on the number and types of fittings on a tank. Only the average roof fitting loss factors have been included in this Appendix.

C. Internal Floating Roof Tanks

The equations provided in this section are applicable only to freely vented internal floating roof tanks. These equations are not intended to estimate losses from closed internal floating roof tanks (tanks vented only through a pressure/vacuum vent).

Emissions from internal floating roof tanks may be estimated as:

$$L_T = L_S + L_W + L_F + L_D$$

where

L_T = total loss, kg/y
L_S = rim seal loss
L_W = withdrawal loss, kg/y
L_F = deck fitting loss, kg/y
L_D = deck seam loss, kg/y

1. Seal Loss

Rim seal losses (L_S) are calculated in the same way as for external floating roof tanks. However, for internal floating roof tanks, use the following K_s and n values:

SEAL	WELDED TANK	
SEAL TYPE	K_s	n
Liquid mounted resilient seal		
Primary seal only	3.0	0
With rim mounted secondary seal	1.6	0
Vapour mounted resilient seal		
Primary seal only	6.7	0
With rim mounted secondary seal	2.5	0

If tank specific information is not available about the secondary seal on an internal floating roof tank, then assume only a primary seal is present.

2. Deck Fitting Loss

The losses from deck fittings may be calculated from the equation:

$$L_F = P^* M_v K_c F_f$$

where

L_F = deck fitting loss from the tank (kg/yr)

$P^* = \dfrac{P/P_{amb}}{(1 + (1 - P/P_{amb})^{0.5})^2}$

M_v = vapour molecular weight (g/mol)

K_c = a factor to adjust for crude oil storage
= 1 for organic chemicals

F_f = deck fitting factor (kg-mol/yr)

The following general equations from AP-42 should be used to estimate F_f from the tank diameter:

	F_f, kg-mol/yr	
TANK TYPE	WELDED DECKS	BOLTED DECKS
Roof with column support	$.1879D^2 + 2.072D + 60.87$	$0.235D^2 + 2.072D + 60.87$
Roof, self-supporting	$0.0644D^2 + 1.176D + 47.72$	$0.111D^2 + 1.176D + 47.72$

3. Deck Seam Loss

Internal floating roof tanks with welded decks do not have deck seam losses.

For bolted decks, losses are calculated by the equation:

$$L_D = K_D S_D D^2 P^* M_v K_c$$

where

LD = deck seam loss (kg/yr)
K_D = deck seam loss per unit seam length (kg-mol/m yr)
= 0 for welded decks
= 0.506 for bolted deck
S_D = deck seam length factor (m/m^2)
= length of seam/area of deck

D, P*, M_v and K_c as defined for external floating roof tanks. Typical deck seam factors are:

	S_D (m/m^2)
Continuous sheet construction	
1.5 m wide sheets	0.66
1.8 m wide sheets	0.56
2.1 m wide sheets	0.46
Panel construction	
1.5 x 2.3 m rectangular	1.08
1.5 x 3.7 m rectangular	0.92

Where tank specific deck seam length factors are not available assume a value of 0.66 m/m^2, which represents common decks in use.

4. Withdrawal Loss

The working loss from an internal floating roof tank is somewhat higher than that for an external floating roof tank if the roof is supported by columns because of the extra wetted surface. The equation for loss is:

$$L_w = 0.004 \frac{C W_l [1 + (N_c F_c / D)] Q}{D}$$

where

L_w - withdrawal loss from the tank (kg/yr)
C - clingage factor as in the case for the external floating roof tank ($m^3/1000\ m^2$)
W_l - liquid density (kg/m^3)
D - tank diameter (m)
N_c - number of columns
F_c - effective column diameter (m)
- perimeter/π
Q - annual working throughput (m^3). This is the throughput which results in raising and lowering of the internal floating roof.

When N_c is zero, the loss equation is identical to that for the external floating roof tank.

As in the previous tanks, the product parameters must be calculated at the tank temperature.

D. Horizontal Tanks

Very approximate estimates of emissions from horizontal fixed roof tanks can be made using the method described earlier for upright fixed roof tanks. If a user needs to estimate emissions from a horizontal fixed roof tank, some of the tank parameters can be modified before using the vertical tank equations. First, by assuming that the tank is one-half filled, the surface area of the liquid in the tank is approximately equal to the length of the tank times the diameter of the tank. Next, assume that this area represents a circle, i.e., that the liquid is in an upright cylinder. The diameter of that circle can be solved for and used in the equations as D. One-half of the diameter of horizontal tank should be used as the value for H.

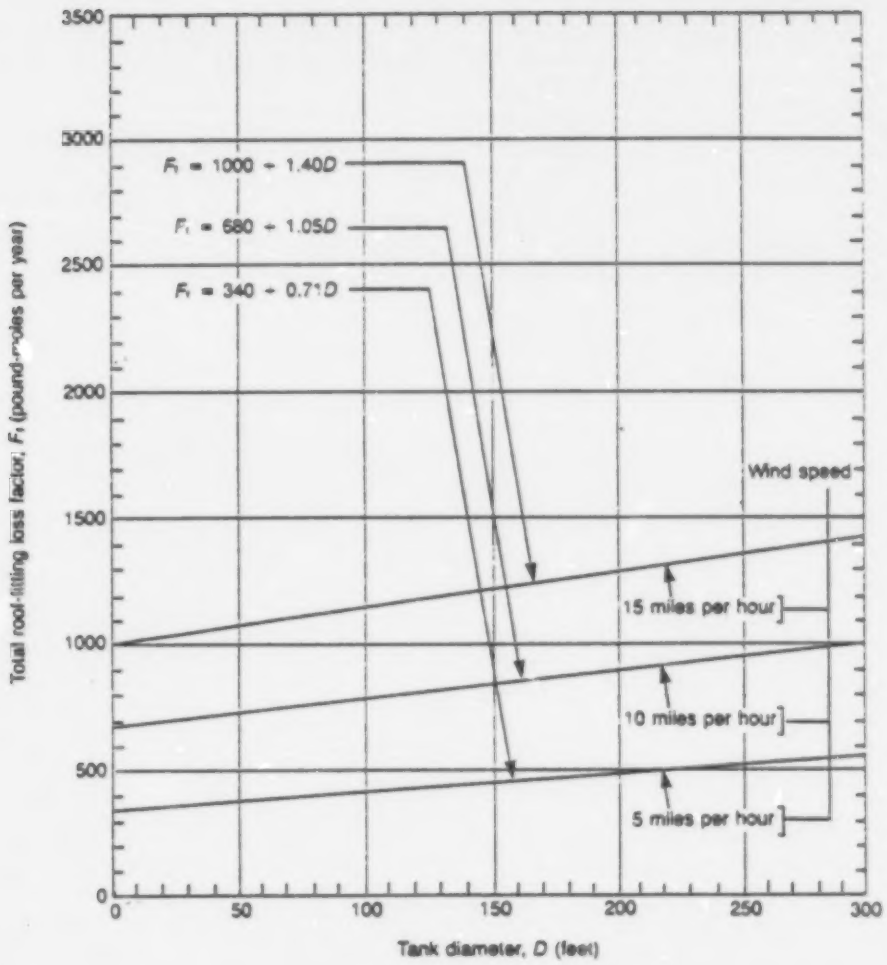


FIGURE IV-1 TOTAL ROOF-FITTING LOSS FACTOR FOR TYPICAL FITTINGS ON PONTOON FLOATING ROOFS

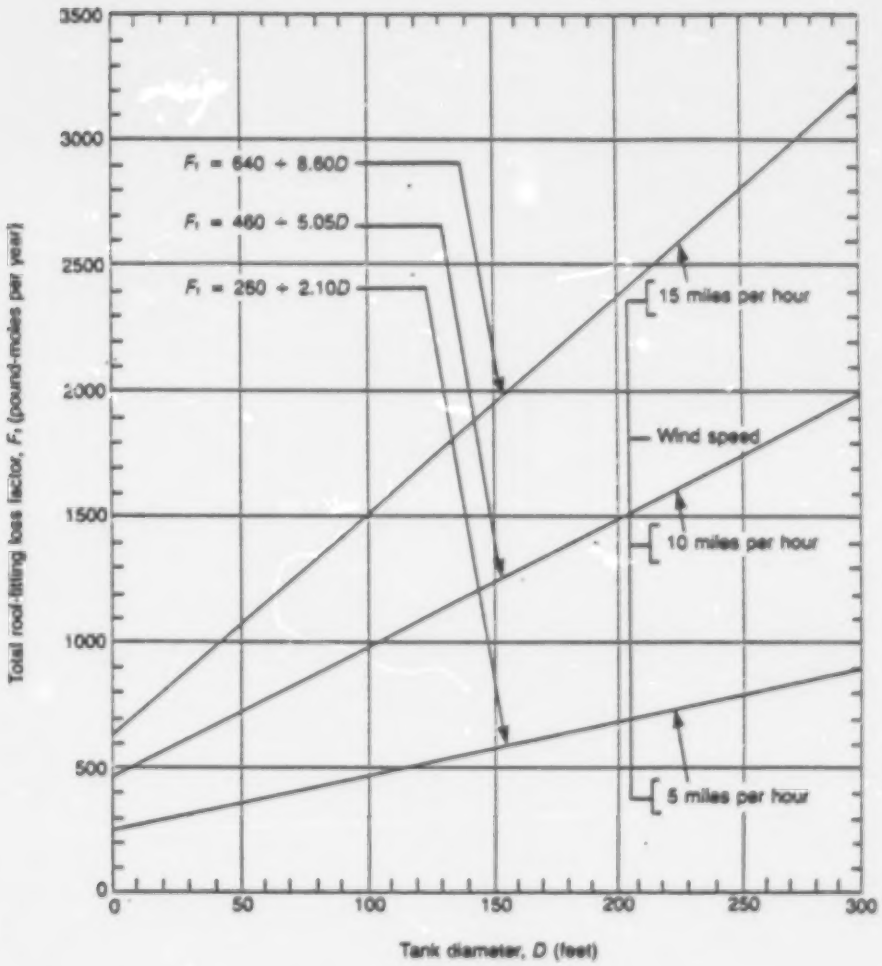


FIGURE IV-2 TOTAL ROOF-FITTING LOSS FACTOR FOR TYPICAL FITTINGS ON DOUBLE-DECK FLOATING ROOFS

Physical Properties of Selected Petrochemicals

Name	Formula	Molecular Weight	Boiling Point at 1 Atmosphere (degrees Fahrenheit)	Liquid Density at 60°F (pounds per gallon)	Vapor Pressure (pounds per square inch absolute) at 40°F	50°F	60°F	70°F	80°F	90°F	100°F
Acetone	CH_3COCH_3	58.08	133.0	6.628	1.682	2.185	2.862	3.713	4.699	5.917	7.251
Acetonitrile	CH_3CN	41.05	178.9	6.558	0.638	0.831	1.083	1.412	1.876	2.456	3.133
Acrylonitrile	CH_2:$CHCN$	53.06	173.5	6.758	0.812	0.967	1.373	1.779	2.378	3.133	4.022
Allyl alcohol	CH_2:$CHCH_2OH$	58.08	206.6	7.125	0.135	0.193	0.261	0.387	0.522	0.716	1.086
Allyl chloride	CH_2:$CHCH_2Cl$	76.53	113.2	7.864	2.998	3.772	4.797	6.015	7.447	9.110	11.025
Ammonium hydroxide (28.8% solution)	$NH_4OH—H_2O$	35.05	83.0	7.481	5.130	6.630	8.481	10.760	13.520	16.760	20.680
Benzene	C_6H_6	78.11	176.2	7.365	0.638	0.870	1.160	1.508	1.972	2.610	3.287
iso-Butyl alcohol	$(CH_3)_2CHCH_2OH$	74.12	227.1	6.712	0.058	0.097	0.135	0.193	0.271	0.387	0.541
tert-Butyl alcohol	$(CH_3)_3COH$	74.12	180.5	6.595	0.174	0.290	0.425	0.638	0.909	1.238	1.702
n-Butyl chloride	$CH_3CH_2CH_2CH_2Cl$	92.57	172.0	7.430	0.715	1.006	1.320	1.740	2.185	2.684	3.481
Carbon disulfide	CS_2	76.13	115.3	10.588	3.036	3.867	4.834	6.014	7.387	9.185	11.215
Carbon tetrachloride	CCl_4	153.84	170.2	13.366	0.793	1.064	1.412	1.798	2.301	2.997	3.771
Chloroform	$CHCl_3$	119.39	142.7	12.488	1.528	1.934	2.475	3.191	4.061	5.163	6.342
Chloroprene	CH_2:CCl-CH:CH_2	88.54	138.9	8.046	1.760	2.320	2.901	3.655	4.563	5.685	6.981
Cyclohexane	C_6H_{12}	84.16	177.3	6.522	0.677	0.928	1.218	1.605	2.069	2.610	3.249
Cyclopentane	C_5H_{10}	70.13	120.7	6.248	2.514	3.287	4.177	5.240	6.517	8.063	9.868
1,1-Dichloroethane	CH_3CHCl_2	98.97	135.1	9.861	1.682	2.243	2.901	3.771	4.738	5.840	7.193
1,2-Dichloroethane	CH_2ClCH_2Cl	98.97	182.5	10.500	0.561	0.773	1.025	1.431	1.740	2.243	2.804
cis-1,2-Dichloroethylene	$CHCl$:$CHCl$	96.95	140.2	10.763	1.450	2.011	2.668	3.461	4.389	5.646	6.803
trans-1,2-Dichloroethylene	$CHCl$:$CHCl$	96.95	119.1	10.524	2.552	3.384	4.351	5.530	6.803	8.315	10.016
Diethylamine	$(C_2H_5)_2NH$	73.14	131.9	5.906	1.644	1.992	2.862	3.867	4.892	6.130	7.541
Diethyl ether	$C_2H_5OC_2H_5$	74.12	94.3	5.988	4.215	5.666	7.019	8.702	10.442	13.342	Deaths
Di-*iso*-propyl ether	$(CH_3)_2CHOCH(CH_3)_2$	102.17	153.5	6.075	1.199	1.586	2.127	2.746	3.481	4.254	5.298
1,4-Dioxane	O-$CH_2CH_2OCH_2CH_2$	88.10	214.7	8.659	0.232	0.329	0.425	0.619	0.831	1.141	1.568
Dipropyl ether	$CH_3CH_2CH_2OCH_2CH_2CH_3$	102.17	195.8	6.260	0.425	0.619	0.831	1.102	1.431	1.876	2.329
Ethyl acetate	$C_2H_5OOCCH_3$	88.10	170.9	7.551	0.580	0.831	1.102	1.489	1.934	2.514	3.191
Ethyl acrylate	C_2H_5OOCCH:CH_2	100.11	211.8	7.750	0.213	0.290	0.425	0.599	0.831	1.122	1.470

Continued

Name	Formula	Molecular Weight	Boiling Point at 1 Atmosphere (degrees Fahrenheit)	Liquid Density at 60°F (pounds per gallon)	Vapor Pressure (pounds per square inch absolute) at 40°F	50°F	60°F	70°F	80°F	90°F	100°F
Ethyl alcohol	C_2H_5OH	46.07	173.1	6.610	0.193	0.406	0.619	0.870	1.218	1.682	2.320
Freon 11	CCl_3F	137.38	75.4	12.480	7.032	8.804	10.900	13.40	16.31	19.69	23.60
n-Heptane	$CH_3(CH_2)_5CH_3$	100.20	209.2	5.727	0.290	0.406	0.541	0.735	0.967	1.238	1.586
n-Hexane	$CH_3(CH_2)_4CH_3$	86.17	155.7	5.527	1.102	1.450	1.876	2.436	3.055	3.906	4.892
Hydrogen cyanide	HCN	27.03	78.3	5.772	6.284	7.831	9.514	11.853	15.392	18.563	22.237
Isooctane	$(CH_3)_3CCH_2CH(CH_3)_2$	114.22	210.6	5.794	0.213	0.387	0.580	0.812	1.093	1.392	1.740
Isopentane	$(CH_3)_2CHCH_2CH_3$	72.15	82.1	5.199	5.878	7.889	10.005	12.530	15.334	18.370	21.657
Isoprene	$(CH_2):C(CH_3)CH:CH_2$	68.11	93.5	5.707	4.757	6.130	7.677	9.668	11.699	14.503	17.113
Isopropyl alcohol	$(CH_3)_2CHOH$	60.09	180.1	6.573	0.213	0.329	0.483	0.677	0.928	1.296	1.779
Methacrylonitrile	$CH_2:C(CH_3)CN$	67.09	194.5	6.738	0.483	0.657	0.870	1.160	1.470	1.934	2.456
Methyl acetate	CH_3OOCCH_3	74.08	134.8	7.831	1.489	2.011	2.746	3.693	4.699	5.762	6.961
Methyl acrylate	$CH_2OOCCH:CH_2$	86.09	176.9	7.996	0.599	0.773	1.025	1.354	1.798	2.398	3.055
Methyl alcohol	CH_3OH	32.04	148.4	6.630	0.735	1.006	1.412	1.953	2.610	3.461	4.525
Methylcyclohexane	$CH_3\text{-}C_6H_{11}$	98.18	213.7	6.441	0.309	0.425	0.541	0.735	0.986	1.315	1.721
Methylcyclopentane	$CH_3C_5H_9$	84.16	161.3	6.274	0.909	1.160	1.644	2.224	2.862	3.616	4.544
Methylene chloride	CH_2Cl_2	84.94	104.2	11.122	3.094	4.254	5.434	6.787	8.702	10.329	13.342
Methyl ethyl ketone	$CH_3COC_2H_5$	72.10	175.3	6.747	0.715	0.928	1.199	1.489	2.069	2.668	3.345
Methyl methacrylate	$CH_2OOCC(CH_3):CH_2$	100.11	212.0	7.909	0.116	0.213	0.348	0.541	0.773	1.064	1.373
Methyl propyl ether	$CH_3OC_3H_7$	74.12	102.1	6.166	3.674	4.738	6.091	7.058	9.417	11.602	13.729
Nitromethane	CH_3NO_2	61.04	214.2	9.538	0.213	0.251	0.348	0.503	0.715	1.006	1.334
n-Pentane	$CH_3(CH_2)_3CH_3$	72.15	96.9	5.253	4.293	5.454	6.828	8.433	10.445	12.959	15.474
n-Propylamine	$C_3H_7NH_2$	59.11	119.7	6.030	2.456	3.191	4.157	5.250	6.536	8.044	9.572
1,1,1-Trichloroethane	CH_3CCl_3	133.42	165.2	11.216	0.909	1.218	1.586	2.030	2.610	3.307	4.199
Trichloroethylene	$ClHC:CCl_2$	131.40	188.6	12.272	0.503	0.677	0.889	1.180	1.508	2.030	2.610
Toluene	$CH_3\text{-}C_6H_5$	92.13	231.1	7.261	0.174	0.213	0.309	0.425	0.580	0.773	1.006
Vinyl acetate	$CH_2:CHOOCCH_3$	86.09	162.5	7.817	0.735	0.986	1.296	1.721	2.262	3.113	4.022
Vinylidene chloride	$CH_2:CCl_2$	96.5	89.1	10.383	4.990	6.344	7.930	9.806	11.799	15.280	23.210

Note: Most of the values in this table were taken or calculated from data given in J. Timmermanns, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier, New York, 1950, and in R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick (Eds.), *Chemical Engineers Handbook* (4th ed.), McGraw-Hill, New York, 1963.

APPENDIX V

EQUATIONS FOR CALCULATION OF

VOC EMISSIONS FROM PRODUCT LOADING OPERATIONS

VOC emissions occur while loading bulk carriers such as tank trucks, rail cars and marine vessels. Correlations have been developed by the U.S. EPA for gasoline loading operations but none exist specifically for organic chemicals.

1. Tank Trucks and Rail Cars

The emissions of organic chemicals from loading of tank trucks and rail cars are to be approximated using the relationship:

$$L_v = 0.00966 \times \frac{12.46\ S\ P\ M_v\ Q}{(T + 273.15)}$$

where

L_v - vehicle loading loss (kg/yr)
S - normalized saturation factor to account for the effects of how the vehicle is loaded
P - true vapour pressure at temperature (kPa)
M_v - vapour molecular weight (g/mol)
T - bulk temperature (°C)
Q - annual volume loaded (m^3)

Values for S are as follows:

Splash Loading

Clean cargo tank	1.45
Dedicated normal service	1.45
Dedicated vapour balance service	1.0

Submerged Loading

Clean cargo tank	0.5
Dedicated normal service	0.6
Dedicated vapour balance service	1.0

Emissions from controlled loading operations should be calculated by multiplying the uncontrolled emission calculated as above by the control efficiency term:

$$\frac{(100 - \text{control efficiency})}{100}$$

2. Barge and Ship Loading

Methodologies do not exist for estimating VOC emissions from loading of marine vessels for organic chemicals. Emission factors are available for gasoline and crude oil, but these cannot be adapted and used for organic chemicals in Canada.

CCPA/ENVIRONMENT CANADA SURVEY OF ATMOSPHERIC EMISSIONS OF VOLATILE ORGANIC COMPOUNDS IN 1988 FROM SELECTED ORGANIC CHEMICAL PLANTS:

DATA SHEETS

Company Name _____

Site Address _____

_____

_____

Site Location Latitude _____ Longitude _____

Mailing Address _____

_____

_____

Liaison Officer _____

Telephone Number _____ Facsimile Number _____

Date _____, 1989

RETURN TO: B.H. Levelton & Associates Ltd.
8805 Osler Street
Vancouver, B.C.
V6P 4G1

Attention: Mr. W.C. Edwards

TABLE 1 DESCRIPTION OF VOC CONTROL SYSTEM

I.D. from Process Diagram _____ System Name _____

General Description and Uses of Control System: _____

_____

_____

_____

_____

_____

Technology used: _____

_____

_____

_____

_____

VOC Control Efficiency:

List Input Chemicals[a]	Control Efficiency (%)	Circle Basis for Value[b]			
_____	_____	M	S	E	O
_____	_____	M	S	E	O
_____	_____	M	S	E	O
_____	_____	M	S	E	O

Annual Overall VOC Control Efficiency[c]: _____

State conditions when input streams bypass controls, the impacts of this on emissions and approximate percent availability of controls: _____

_____

_____

_____

_____

_____

Remarks: _____

_____

_____

_____

_____

[a] Provide any available data for chemicals on the Priority Substances List (Appendix I), particularly benzene, toluene, xylenes and styrene.

[b] M measured; S supplier; E engineering estimate; O other - please explain

[c] Allow for upsets, variability of performance and time the flow bypasses the control unit.

TABLE 2 SUMMARY OF PROCESS EMISSIONS CALCULATED USING EMISSION FACTORS

SOURCE DESCRIPTION	A BASE QUANTITY[1] (tonnes/yr)	B EMISSION FACTOR (kg/tonne) EPA[2]	B EMISSION FACTOR (kg/tonne) OTHER[3]	CONTROL I.D.	C CONTROL EFFICIENCY[4] (%)	ANNUAL EMISSION A x B x (100-C)/100 (kg/yr)	COMPOSITION OF EMITTED VOC (wt %) BENZ	TOLU	XYL	STY	OTHER[5]	COMMENTS AND STACK[6] HEIGHT IF ≥ 30 m

REMARKS:

Notes:

1 Units of base quantities are given in Appendix II.
2 Uncontrolled emission factor from Appendix II for each source.
3 Alternate emission factor. Give reference and justification on separate sheet.
4 VOC removal efficiency for controls on discharges from sources.
5 Benzene, Toluene, Xylenes, Styrene, other Priority Substances from Appendix I.
6 Make note of comments on the calculated emission here or on separate page.

TABLE 3 SUMMARY OF PROCESS EMISSIONS CALCULATED USING SPECIFIC SOURCE DATA

SOURCE DESCRIPTION	A FLOW RATE (m^3/h)	B HOURS PER YEAR	C VOC CONCENTRATION (g/m^3)	CONTROL I.D.	D CONTROL EFFICIENCY[1] (%)	E ANNUAL[2] VOC EMISSION (kg)	COMPOSITION OF EMITTED VOC (wt %) BENZ	TOLU	XYL	STY	OTH[3]	COMMENTS AND[4] STACK HEIGHT IF ≥ 30 m

REMARKS:

Notes:

[1] VOC removal efficiency for controls on discharges from sources

[2] Annual emission, $E = A \times B \times C/1000 \times \frac{(100-D)}{100}$ kg

[3] Benzene, Toluene, Xylenes, Styrene, Other Priority Substances from Appendix I

[4] Give assumptions and sources of data here or on separate page

TABLE 4 SUMMARY OF EMISSION FROM INTERMITTENT PROCESS SOURCES CALCULATED USING SPECIFIC SOURCE DATA[4]

SOURCE DESCRIPTION	A FLOW RATE (m^3/h)	B HOURS PER YEAR	C VOC CONCENTRATION (g/m^3)	CONTROL I.D.	D CONTROL EFFICIENCY[1] (%)	E ANNUAL[2] VOC EMISSION (kg)	COMPOSITION OF EMITTED VOC (wt %) BENZ	TOLU	XYL	STY	OTH[3]	COMMENTS[4]

REMARKS:

Notes:

[1] VOC removal efficiency for controls on discharge from sources

[2] Annual emission, $E = A \times B \times C/1000 \times \frac{(100-D)}{100}$ kg

[3] Benzene, Toluene, Xylenes, Styrene, Other Priority Substances from Appendix I

[4] Give assumptions and sources of data here or on separate page

TABLE 5A MARY OF FUGITIVE VOLATILE ORGANIC COMPOUND EMISSIONS FOR UNIT PROCESSES AND TOTAL PLANT

Unit Process I.D.: _____ Unit Process Name or Total Plant: _____

SOURCES	SERVICE AND SEAL TYPE	NUMBER	COMPOSITION (wt %)[1]						EMISSION FACTORS kg/h/source			ANNUAL HOURS[2]	TOTAL ANNUAL VOC EMISSIONS kg
		A	BENZ.	TOLU.	XYL.	STY.	OTH	OTH	SOCNI B	LEAK	NO LEAK	C	A x B x C
1. Valves[3]	Gas								0.0056				
	Light Liquid								0.0071				
	Heavy Liquid								0.00023				
2. Pump Seals	Light Liquid								0.0494				
	Canned												
	Packed												
	Single Mech.												
	Double Mech.												
	Other (Specify)												
	Heavy Liquid								0.0214				
	Canned												
	Packed												
	Single Mech.												
	Double Mech.												
	Other (Specify)												
3. Compressor Seals	Gas/Vapour								0.228				
	Labyrinth												
	Mechanical												
	Segmented												
	Dry												
	Other (Specify)												
4. Pressure Relief Seals	Gas/Vapour								0.104				
5. Flanges	All								0.00083				
6. Open Ended Lines	All								0.0017				
7. Sampling Connections	All								0.0150				
TOTAL													

REMARKS:

NOTES:

1 Benzene, toluene, xylenes, styrene, other priority substances from Appendix I
2 Annual hours = 8760 unless noted
3 Exclude valves less than 1/2 inch

TABLE 5B

VALVE SCREENING DATA

PLANT IDENTIFICATION													COMPOSITION (%) *									
INTERNAL PLANT IDENTIFICATION		SYSTEM																				
VALVE NUMBER *			CLASS	MODE	TYPE	PACKING	MANU	MODEL	SIZE	PRESS	TEMP	ACCES	SERVICE *	BENZ	TOLU	XYL	STY	OTH			MAX SV	INSTR

I. Valves Data Sheet Key

Variable	Description
Mode	Mode of Control: A = Automatic M = Manual
Equip	Equipment Type: Ga = Gate Gl = Globe Ba = Ball Pl = Plug Bu = Butterfly Ne = Needle Di = Diaphragm O = Other (Specify)
Pack	Packing Material (If Any):
Manu	Manufacturer:
Model	Model:
Size	Line Size Diameter in Inches
Press	Pressure (Units _____)
Temp	Temperature in Degrees Farenheit
Acc	Accessible: Y = Yes N = No
Serv	Service: G = Gas/Vapor L = Light Liquid H = Heavy Liquid
Stream Composition	Weight Percentage of Each Compound in the Line
Max. SV	Maximum Uncorrected Screening Value

TABLE 5C

PUMP SCREENING DATA

PLANT IDENTIFICATION / INTERNAL PLANT IDENTIFICATION SYSTEM													COMPOSITION (%)									
PUMP NUMBER			EQU.	SEAL	PACK.	FLUID	MANU	MODEL	SIZE	PRESS.	TEMP	ACCES	SERVICE	BENZ	TOLU	XYL	STY	OTH			MAX SV	INSTR.
*				*									*									

2. Pumps Data Sheet Key

Variable	Description
Equip	Equipment Type: P = Piston C = Centrifugal O = Other (Specify)
Seal	Seal Type: C = Canned P = Packed S = Single Seal D = Dual Seal O = Other (Specify)
Pack	Packing Material (Packed Seals Only):
Fluid	Barrier Fluid (Dual Seals Only):
Manu	Manufacturer:
Model	Model:
Size	Size in Gallons Per Minute
Press	Pressure (Units_____)
Oper	Operating: Y = Yes (On) N = No (Off)
Acc	Accessible: Y = Yes N = No
Serv	Service: L = Light Liquid H = Heavy Liquid
Stream Composition	Weight Percentage of Each Compound in the Line
Max. SV	Maximum Uncorrected Screening Value

TABLE 5D

COMPRESSOR SCREENING DATA

PLANT IDENTIFICATION																		
INTERNAL PLANT IDENTIFICATION SYSTEM																		
COMP NUMBER			EQUIP	SEAL	PRESSURE	ACCESSIBLE	COMPOSITION (%) SERVICE	BENZ.	TOLU.	XYL.	STY	OTH			MAX SV	INSTR

3. Compressors Data Sheet Key

Variable	Description
Equip	Equipment Type: P = Piston C = Centrifugal O = Other (Specif
Seal	Seal Type: L = Labrynth M = Mechanical S = Segmented D = Dr O = Other (Specify)
Press	Line Pressure (Units _____)
Acc	Accessible: Y = Yes N = No
Stream	
Composition	Weight Percentage of Each Compound in the Line
Max. SV	Maximum Uncorrected Screening Value

TABLE 5E

PRV SCREENING DATA

PLANT IDENTIFICATION / INTERNAL PLANT IDENTIFICATION SYSTEM															COMPOSITION (%) *								MAX SV	INSTR
PRV. NUMBER *			CLASS	DISC	CONT.	SEAT	CHECK	SIZE	P-SET	P-OPR	TEMP.	ACCES	REL. PT.	SERVICE	BENZ.	TOLU.	XYL.	STY	OTH				

A-22

4. PRVs Data Sheet Key

Variable	Description
Disk	Disk: Y = Yes N = No
Cont	Control Device: Y = Yes N = No
Seat	Seat Type: H = Hard S = Soft
Check	Period Between Regular Checks of Set Point (Units _____) (Blank = No Regular Checks)
Size	Line Size Diameter in Inches
P-Set	Set Point Pressure (Units _____)
P-Opr	Operating Pressure (Units _____)
Temp	Temperature in Degrees Farenheit
Acc	Accessible: Y = Yes N = No
Stream Composition	Weight Percentage of Each Compound in the Line
Max. SV	Maximum Uncorrected Screening Value
Rel. Pt	Release Point: - F - Flare A - Atmosphere C - Closed System

TABLE 5F

CONNECTION SCREENING DATA

PLANT IDENTIFICATION										COMPOSITION (%) *									
INTERNAL PLANT IDENTIFICATION SYSTEM																			
CONNECTION NO: *			CLASS	EQUIP.	GASKET	INSUL.	SIZE	TEMP.	ACCES.	SERVICE	BENZ.	TOLU.	XYL.	STY	OTH			MAXSV	INSTR

5. Connections Data Sheet Key

Variable	Description
Equip	Equipment Type: S = Screwed B = Bolted (FLANGES)
Gask	Gasket Material:
Insul	Insulation: Y = Yes N = No
Size	Line Size Diameter in Inches
Temp	Line Temperature in Degrees Farenheit
Acc	Accessible: Y = Yes N = No
Stream Composition	Weight Percentage of Each Compound in the Line
Max. SV	Maximum Uncorrected Screening Value

TABLE 5G

OPEN ENDED LINE SCREENING DATA

PLANT IDENTIFICATION							COMPOSITION (%) *									
INTERNAL PLANT IDENTIFICATION SYSTEM																
O.E. LINE NO.:			I.L.V. MANU.	I.L.V. MODEL	SIZE	ACCESSIBLE	SERVICE	BENZ.	TOLU.	XYL.	STY	OTH			MAX.SV	INSTR.
*																

6. Open-Ended Lines Data Sheet Key

Variable	Description
ILV Manu	In-Line Valve Manufacturer:
ILV Model	In-Line Valve Model:
Size	Line Size Diameter in Inches
Acc	Accessible: Y = Yes N = No
Stream Composition	Weight Percentage of Each Compound in the Line
Max. SV	Maximum Uncorrected Screening Value

ABLE 6 EMISSIONS FROM FIXED ROOF TANKS

ANK ID	PRODUCT STORED	DIAMETER D (m)	VAPOUR HEIGHT H_V (m)	TRUE[2] VAPOUR PRESSURE P (kPa)	ΔT (°C)	M_v (g/mol)	F_p	C_d (m^3)	THROUGHPUT Q (m^3)	K_t (m^3)	ANNUAL EMISSIONS[1] BREATHING L_s (kg)	WORKING L_w (kg)	TOTAL (kg)	COMPOSITION OF EMITTED VOC (wt %) BENZ	TOLU	XYL	STY	OTH[3]

Notes:

See Appendix IV for emission equations
P_{amb} - _____ kPa
Benzene, toluene, xylenes, styrene, Other priority Substances from Appendix I.

TABLE 6a EMISSIONS FROM OTHER (FIXED ROOF) TANKS[1]

TANK ID	PRODUCT STORED	DIAMETER D (m)	VAPOUR HEIGHT H_v (m)	TRUE[2] VAPOUR PRESSURE P (kPa)	ΔT (°C)	M_v (g/mol)	F_p	C_c (m^3)	THROUGHPUT Q (m^3)	K_t (m^3)	ANNUAL EMISSIONS[3] BREATHING L_b (kg)	WORKING L_w (kg)	TOTAL (kg)	COMPOSITION OF EMITTED VOC (wt %) BENZ	TOLU	XYL	STY	OTH[4]

Notes:

[1] Include horizontal above-ground and underground tanks, but exclude spherical and bullet tanks
[2] See Appendix IV for emission equations for horizontal tanks (p IV-10)
[3] P_{atm} - _____ kPa
[4] Benzene, toluene, xylenes, styrene, Other priority Substances from Appendix I.

ABLE 7 EMISSIONS FROM EXTERNAL FLOATING ROOF TANKS

ANK ID	PRODUCT STORED	DIAMETER	TRUE[2] VAPOUR PRESSURE	p*	WIND SPEED	n	M_v	K_s	C	W_l	F_f	THROUGHPUT		ANNUAL EMISSIONS[1]				COMPOSITION OF EMITTED VOC (wt %)				
												WORKING	TOTAL	SEAL	WORKING	FITTING	TOTAL					
		D	P		V							Q		L_s	L_w	L_{Rf}						
		(m)	(kPa)		(km/h)		(g/mol)		$\frac{m^3}{1000m^2}$	$\frac{(kg)}{m^3}$		(m^3)	(m^3)	(kg)	(kg)	(kg)	(kg)	BENZ	TOLU	XYL	STY	OTH[3]

Notes:

See Appendix IV for emission equations
P_{atm} = _____ kPa
Benzene, Toluene, Xylenes, Styrene, Other Priority Substances from Appendix I

TABLE 8 EMISSIONS FROM INTERNAL FLOATING ROOF TANKS

TANK ID	PRODUCT STORED	DIAMETER D (m)	TRUE[2] VAPOUR PRESSURE P (kPa)	p*	WIND SPEED V (km/h)	n	M_v (g/mol)	K_s	C $\frac{m^3}{1000m^2}$	W_l $\frac{(kg)}{m^3}$	N_cF_c	S_D	F_F	THROUGHPUT WORKING (m^3)	THROUGHPUT TOTAL (m^3)	ANNUAL EMISSIONS[1] SEAL L_s (kg)	FITTING L_f (kg)	WITH-DRAWAL L_W (kg)	SEAM L_D (kg)	TOTAL (kg)	COMPOSITION OF EMITTED VOC (wt %) BENZ	TOLU	XYL	STY	OTH[3]

Notes:

See Appendix IV for emission equations
P_{amb} = _____ kPa
Benzene, Toluene, Xylenes, Styrene, Other Priority Substances from Appendix I

TABLE 9 EMISSION CALCULATIONS FOR LOADING OPERATIONS

CHEMICAL LOADED	MODE OF SHIPMENT[1]	METHOD OF LOADING[2]	A ANNUAL QUANTITY (t)	AVERAGE TEMPERATURE (°C)	TRUE VAPOUR PRESSURE (kPa)	B EMISSION FACTOR[3] (kg/t)	C CONTROL EFFICIENCY (%)	ANNUAL EMISSION $A * B * \frac{(100-C)}{100}$ (kg)

Notes:

1 Tank truck (T), rail tank car (R), barge (B), tanker ship (S).
2 Splash loading (S), Submerged loading (B).
3 Calculate using equations given in Appendix V.

TABLE 10 SPILLS/ACCIDENTAL DISCHARGES OF VOCs FOR PREVIOUS 3 YEARS[1]

DATE	PROCESS UNIT	EVENT	DURATION	VOC EMITTED	COMPOSITION OF EMITTED VOC (wt %)				
			(hours)	(kg)	BENZ	TOLU	XYL	STY	OTH[2]
Total Emission for 3 year period									
Average Annual Emission (total/3)									

Notes:

1 For liquid spills estimate the amount of VOC emitted to atmosphere
2 Benzene, Toluene, Xylenes, Styrene, Other Priority Substances from Appendix I

APPENDIX B

FUGITIVE EMISSION CONTROL PROGRAMS AT SEVERAL SURVEYED COMPANIES

VALVES:

- Fugitive emission detection has been ongoing with survey's being carried out before shutdown by operator observation - due to smell or frosting of valves etc.
- Fugitive emissions are caught if there is welding in the area by a gas detector.
- During shutdowns known leakers have been repacked or replaced.
- New valve packings and replacements are upgraded to flexible graphite type.
- Inject leak sealing compound into packings that cannot be tightened or repacked.

FLANGES:

- Flanges are leak checked on unit startup using nitrogen pressure and soap solution.
- Different types of flange gaskets are being investigated for effectiveness. In particular flexible graphite both eliminates asbestos and reduces fugitive emissions.
- An SQC system for torquing flanges was used in the 1988 shutdown with approximately 5% of the flanges tested. Improvements in practices were made proactively, resulting in no detectable leaks at start-up.
- Flange leaks that cannot be tightened on-line are repaired by installing of clamps with leak sealing compound.

SAFETY RELIEF VALVES (SV):

- Regular maintenance checks are performed on all SV's. Checking interval varies from 6 months to 3 years depending on the service.
- All safety valves that lift are checked or replaced.
- A majority of safety valves are tied into the flare system.
- Pressure dump valves are inspected regularly to minimize any leakage to flare.

OPEN ENDED LINES (OEL):

- All OEL's which include all valved drips and vents are either blanked or plugged.

PUMPS:

- Any leak detection is by operator observation again, leaking seals are changed at the earliest pump shutdown.

COMPRESSORS:

- The main ethylene compressors have a seal gas recovery system to recover leaking gases from the seal oil.

SAMPLING POINTS:

- For routine sampling, gas samples are blown down through the flare, and liquid samples are returned to pump suction wherever possible.

FUGITIVE EMISSION, SPILL PREVENTION AND DETECTION

DESIGN, INSPECTION, OPERATING AND MAINTENANCE PRACTICES:

The prevention and control of fugitive emissions and spills or leaks has many facets and involves the original design of the facility, specifications and standards, operating and maintenance practices and standards.

Many of the programs, practices and standards which serve to control emissions are standard practice in the chemical industry and were originally introduced for safety, fire protection and occupational health reasons.

The following are some feature of the manufacturing facility in which will serve to reduce VOC emissions.

Engineering and Design Stds:

eg: flange face finish specifications
all hydrocarbon relief valves have rupture disks
all hydrocarbon RV's to flare
spiral wound gaskets in hydrocarbon service
double seals on some pumps
seal leak detectors

Inspection and Testing Programs:

eg: comprehensive metallurgical inspection program
Process Hazard Reviews (such as fault tree analysis)
Turnover Inspection of new/altered facilities
computerized Safety Inspection and Testing System

Emergency Systems:

eg: one button shutdown systems
process interlocks and isolation systems
hydrocarbon detectors throughout the plant
operator training

Miscellaneous:

eg: stud torquing specifications for flanges
process equipment pressure testing
operator patrols
routine checks of rupture disk status
all venting, purging for maintenance, etc. is to flare
plugs in unused bleed valves

Fugitive Emissions Control

A. Design Criteria

(i) All rotating equipment in hydrocarbon service employs tandem mechanical seals with a buffered fluid (API-601-Plan 51 is typical) between the seals.

(ii) All seal pots are vented to the flare and equipped with a flow switch to indicate if they are passing.

(iii) All PSV's in hydrocarbon service are vented to the flare, with some being equipped with a rupture disc located upstream of the PSV.

(iv) All storage tanks are equipped with PVRV's and ERV's and kept under a positive nitrogen pad controlled by a PCV.

(v) All waste gaseous hydrocarbon streams are sent to the flare.

(vi) All waste acid gases are incinerated in the firebox of a steam superheater.

B. Operating and Maintenance Practices

(i) All rotating equipment and seals are on a regular PM schedule.

(ii) All control valves are on a regular PM schedule.

(iii) All drains, vents and lines are thoroughly purged to flare before opening for maintenance.

(iv) Flanges are hot-torqued after start-up where appropriate.

(v) Prior to any work being done that could result in an ignition source, the area is checked for hydrocarbons by operations personnel. This is approximately 15 - 20 gas checks per day. All leaks are repaired immediately.

(vi) All drain, vent and sample lines are capped when not in service.

Design features incorporated in the facility aimed to minimize fugitive emissions are:

- Relief valves where practical are vented to flare.
- Vapour recovery are on all benzene storage tanks.
- Sumps on TPI's are covered and vented.
- Floating roofs on tanks with products of high vapour pressure.
- Welded or flanged fittings on pipes in hydrocarbon service as opposed to screwed fittings.
- Closed loop benzene samplers are used.
- Ball type or equally effective valves used.
- Inplant benzene monitoring system in place.
- Use of double mechanical seals on all pumps in benzene service.
- All valves and drains are capped, plugged or double isolated.
- A closed flushing system is used on mechanical equipment in benzene service prior to maintenance.
- Minimize the need for vessel steam-out: when it is required it is initially steamed to flare.
- Strict adherence to standard operating procedures and plans.

Has conducted training and information sessions on environmental management a Part of this information and also part of our license application was the concept of a Clean Operating Philosophy as a normal way of doing things.

A few examples of the activities resulting from the Clean Operating Philosophy are as follows. The general principles are in our Corporate Policy on Health Safety and Environmental Protection.

- Special flushing procedures for equipment handling benzene, ethylbenzene and styrene.
- Minimizing vessel steamout.
- Emission monitoring.
- Proper use of segregated sewer systems.
- Effective waste disposal.

- Reporting of any spills or emissions.
- Effective waste disposal.
- Water, air and soil are to be considered as product streams with specifications which must be met.
- Air and water quality as well as waste disposal will be monitored to ensure compliance with all legislated regulations.